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Evaluation of Methods for the Isolation or Concentration of Organic Substances from Water Using XAD-4 Quaternary Resin

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EVALUATION OF METHODS FOR THE ISOLATION OR CONCENTRATION OF ORGANIC SUBSTANCES FROM WATER USING XAD-4 QUATERNARY RESIN

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16. ABSTRACT

A synthetic resin (Amberlite XAD-4 Quaternary in the OH- form) was evaluated as an adsorption medium for the concentration/isolation of acids, amines, aldehydes, carbohydrates, chlorobiphenyls, esters, hydrocarbons, ketones, phenols, polynuclear aromatic hydrocarbons, and trihalomethanes in drinking water. The approach utilized for this project was the generation of data by maintaining a program to isolate and/or concentrate each organic compound by not less than 50-fold. The adsorption and desorption processes were performed on a small column; however, a scaled-up column was evaluated during three pilot plant experiments.

In general, the XAD-4 Quaternary resin in the hydroxide form was found to be efficient for 50-fold concentrations of 12 of the 22 organic compounds. However, percent recoveries where humic substances and inorganic salts were present, are as low as 15% for bis(2-ethylhexyl)phthalate and as high as 55% for isophorone. Glucose, glycine, stearic acid, furfural and caffeine were among the compounds which could not be concentrated by the XAD-4 Quaternary resin.

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FOREWORD

The many benefits of our modern, developing, industrial society are accompanied by certain hazards. Careful assessment of the relative risk of existing and new man-made environmental hazards is necessary for the establishment of sound regulatory policy. These regulations serve to enhance the quality of our environment in order to promote the public health and welfare and the productive capacity of our Nation's population.

The complexities of environmental problems originate in the deep interdependent relationships between the various physical and biological segments of man's natural and social world. Solutions to these environmental problems require an integrated program of research and development using input from a number of disciplines. The Health Effects Research Laboratory, Research Triangle Park, NC and Cincinnati, OH, conducts a coordinated environmental health research program in toxicology, epidemiology, and clinical studies using human volunteer subjects. Wide ranges of pollutants known or suspected to cause health problems are studied. The research focuses on air pollutants, water pollutants, toxic substances, hazardous wastes, pesticides, and non-ionizing radiation. The laboratory participates in the development and revision of air and water quality criteria and health assessment documents on pollutants for which regulatory actions are being considered. Direct support to the regulatory function of the Agency is provided in the form of expert testimony and preparation of affidavits as well as expert advice to the Administrator to assure the adequacy of environmental regulatory decisions involving the protection of the health and welfare of all U.S. inhabitants.

This report presents the results obtained during the development and evaluation of XAD-4 Quaternary resin as an adsorbent for the isolation and concentration of trace organic substances from water. Methods for the trace enrichment of organic contaminants in water are essential in determining potential health problems associated with waterborne organic contaminants since existing *in vivo* and *in vitro* biological test systems lack the necessary sensitivity for testing water samples as is.

F. Gordon Hueter, Ph.D.
Director
Health Effects Research Laboratory

ABSTRACT

A synthetic resin (Amberlite XAD-4 Quaternary in the OH- form) was evaluated as an adsorption medium for the concentration/isolation of acids, amines, aldehydes, carbohydrates, chlorobiphenyls, esters, hydrocarbons, ketones, phenols, polynuclear aromatic hydrocarbons, and trihalomethanes in drinking water.

The approach utilized for this project was the generation of data by maintaining a program to isolate and/or concentrate each organic compound by not less than 50-fold. The adsorption and desorption processes were performed on a small column; however, a scaled-up column was evaluated during three pilot plant experiments. Studies determining the effect of humic substances and inorganic salts (sodium bicarbonate at 70 ppm, sodium sulfate at 120 ppm, and calcium chloride at 47 ppm) on the adsorption/desorption of the model compounds were also performed in an effort to simulate drinking water conditions.

Because the method developed under this contract is ultimately intended to produce concentrates for biological testing, the effect of a 2 ppm chlorine residual on the generation of chlorinated organic ompounds was studied. In addition, the ability of the method to concentrate lead along with the method compounds was examined since the concentration of heavy metals may interfere with in vivo and in vitro biological tests.

Results of experiments on XAD-4 Quaternary in the presence of salts, but with no humic substances, at 120-150 B.V./hr and for acidic compounds at 48 B.V./hr with and without the presence of salts indicate satisfactory recoveries of most model compounds. Satisfactory recoveries are also indicated at 48 B.V./hr with and without the presence of humic substances except for stearic acid, trimesic acid, and 5-chlorouracil.

In general, the XAD-4 Quaternary resin in the hydroxide form was found to be efficient for 50-fold concentration of 12 of the 22 organic compounds. However, percent recoveries, in pilot study 3 where humic substances and inorganic salts were present, are as low as 15% for bis(2-ethylhexyl)phthalate and as high as 55% for isophorone. In bench scale studies, flow rates in bed volumes were 150 B.V./hr and 48 B.V./hr. Flow rate was 103 B.V./hr in all pilot plant studies. More importantly, the amount of model compounds in the bench scale studies was 3 mg for 10 cm^3 resin and 1500 mg for 200 cm^3 resin in the pilot scale studies.

Glucose, glycine, stearic acid, furfural and caffeine were among the compounds which could not be concentrated by the XAD-4 Quaternary resin. Mass balances developed for each compound indicated that accountability was higher in bench-scale experiments, and a drop of 10 to 20% in accountability was observed in the three pilot plant studies. MIBK, trimesic, quinoline, tetrachlorobiphenyl and bis-(2-ethylhexyl)phthalate showed poor recoveries. Caffeine, which could be concentrated by more than 50-fold in the bench-scale experiment, was not concentrated in the pilot plant studies.

Evaluation of the pilot plant studies suggests that the humic substances, in general, did not affect the concentration of the model compounds with the exception of trimesic acid. The effect of salts appears significant on 1-chlorododecane and 5-chlorauracil, but because of differences between the bench-scale and pilot plant studies, the affect of salts on the concentration of the model compounds is not conclusive.

A chlorine residual of 2 ppm did not generate any new chlorinated compound with the blank XAD-4 Quaternary resin. Lead (at 25 ppb and neutral pH), in the presence of humic substances, was recovered using 0.1N HCl. However, it was found that lead at neutral pH would precipitate as lead sulfate or lead hydroxide.

Breakthrough studies determined for the bench-scale experiments were valuable in the evaluation of the effects of flow rate. Quinaldic acid breakthrough studies indicated that the flow rate had to be reduced from 150 B.V./hr to approximately 48 B.V./hr for the same internal diameter column of 1.0 cm.

The XAD-4 Quaternary resin was also evaluated in the bisulfite form (HSO^{-}_{3}). It was believed that glucose and furfural could be concentrated by the HSO^{-}_{3} functional group. Furfural was shown to be concentrated with an average recovery of approximately 65%, but glucose could not effectively be concentrated from water.

Two other resins, XE-340 for the concentration of chloroform and XN-1010 for the concentration of caffeine, 5-chlorouracil and glycine, were evaluated. It was found that chloroform could be adsorbed on XE-340, but desorption with ether did not result in more than 15% recovery. The XN-1010 resin showed no significant concentration of caffeine or 5-chlorouracil, and glycine results were scattered in a triplicate bench-scale study.

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LIST OF ABBREVIATIONS

AA	Atomic Absorption
BEHP	bis(2-ethylhexyl)phthalate
BHT	2,6-di-tert-butyl-4-methylphenol
B.V.	Bed Volumes
CI	Confidence Interval
ECD	Electronic Capture Detector
FID	Flame Ionization Detector
GC-FID	Gas Chromatography-Flame Ionization Detector
HPLC	High Performance Liquid Chromatography
ID	Inside Diameter
K-D	Kuderna-Danish
PMPS	Polymethyl Polysiloxanes
ppb	parts per billion
ppm	parts per million

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SECTION 1

INTRODUCTION

The field of separation science has made great strides in recent years in developing techniques for isolating, separating and concentrating organic species. One impetus for these advances has been the search for sensitive and accurate analytical methods for trace organics. A second has been the need for effective concentration and isolation techniques for preparing biologically active substances for bio-medical investigations. The objective of this project was directed toward the latter application.

Within the realm of analytical separation systems, by far the most fruitful approach has been in the use of solid sorbent techniques. Although other approaches have been studied (reverse osmosis, solvent extraction, foam separation, etc.), none is so versatile and offers so much potential for selectivity, concentration and field-use as adsorption techniques. This project dealt only with the investigation of adsorbents for the isolation of organic substances for toxicological testing. Furthermore, it was limited to the investigation of newly-developed synthetic sorbents such as the polymeric XAD-4 Quaternary anion exchange resin adsorbent rather than traditional activated carbons.

Our goal for this project was to develop a system for sampling 500 liters (or more) of drinking water which might contain 1 to 50 ppb concentration of organic compounds. Mass balances for each compound have been determined to reveal the unrecovered amount of each compound. The mass balance determinations were required to determine whether recovery losses were the result of volatilization, adsorption, and/or chemical transformation.

Synthetic sorbents are known to contain artifacts in the resin that could be eluted during desorption of the organic compounds concentrated on the resin. Therefore, separate experiments using XAD-4 Quaternary resin (OH^- form) were also performed to evaluate the present of artifacts, either those arising from the interaction of chlorine with the resin or those from the resin itself.

SECTION 2

CONCLUSIONS

The procedure used in this study for the isolation/concentration of organic compounds in drinking water demonstrated that the XAD-4 Quaternary resin (OH^-), is effective for most neutral, acidic and semi-volatile compounds. Because of the Quaternary function of this resin, it was possible to concentrate several acidic compounds without any change in the pH of the sampling water. This is an advantage over normal XAD resins for on-site compositing or grab sampling since the problem of continuous acid addition and subsequent pH monitoring is avoided.

Many classes of organic compounds adsorbed by this resin can be desorbed by solvents such as ether (or acidic methanol and ether). The acidic solvents can be concentrated to remove inorganic acid, but some residual inorganic acid always remained in the concentrated eluants. Residual acid, or possible trace of water in the concentrated eluants, caused analytical variances when methylation was attempted. Therefore, quinaldic acid, trimesic acid and 5-chlorouracil were analyzed by HPLC rather than GC-FID.

Humic substances were concentrated more than 50-fold on the XAD-4 Quaternary resin, but a saturated HCl/methanol solution was required for the desorption. This eluant was not concentrated further because the humic substances' concentration could be measured directly using a spectrophotometer. Total recovery of humic substances was higher in the bench-scale experiments as compared to the pilot plant studies. Based on the pilot plant results (see Summary of Experiment 3), it appears that the adsorption of humic substances were affected by the higher velocity or the loading capacity since 45% was recovered in the effluent water. The higher velocity in the pilot plant studies did not have a similar effect on other compounds such as quinaldic acid, for example, which was recovered at almost 100%. It is believed that caffeine, which was concentrated during bench-scale studies, was also affected by the higher velocity in the pilot plant studies.

The effect of inorganic salts on the concentration of the model compounds appeared to be inconsistent throughout the bench-scale experiments, and several of the model compounds were concentrated less in Pilot Plant Study No. 2.

Results of lead studies indicate that dissolved lead at 25 ppb is not isolated by the XAD-4 Quaternary resin. However, if lead is precipitated in the drinking water sample, the resin acts as a filter, and the precipitated lead compounds collected on the resin can be dissolved by the acidic/methanol eluant. Experiments with the presence of humic substances and lead were conducted since it is known that humic substances can act as chelating agents for heavy metals. Approximately 85% of the lead was recovered, but lead was removed from water due to the initial precipitation of this element. This phenomenon may not occur in actual field sampling since all lead compounds should be a dissolved form.

The XAD-4 Quaternary resin was cleaned by Soxhlet extraction and kept wet under water to minimize artifacts from the resin. An oily, yellow residue observed during concentration of the acidic eluants required an additional cleanup step. Based on results of the resin blank experiments, it was necessary to clean the XAD-4 Quaternary resin by batch process, with saturated HCl/methanol prior to Soxhlet cleaning with solvents. Artifacts such as benzoic acid were found in the resin blank experiments, but in general, the mass of each artifact (per dry weight of resin) was negligible.

The XAD-4 Quaternary resin is recommended for use in concentration (50-fold and higher) of trace organic compounds in water, except for carbohydrates, aldehydes and acidic compounds such as stearic acid and glycine. The breakthrough experiments should be considered for specific compounds to evaluate the effect of mass transfer due to velocity changes. Breakthrough may not occur for large volumes of water samples with trace organic contaminants due to the high capacity of polymeric resins, but high concentrations of specific compounds may breakthrough.

SECTION 3

RECOMMENDATIONS

Future research on the isolation/concentration of organic compounds in water may need to minimize analytical problems by use of radiolabeled compounds.

Based on the results of using several polymeric adsorbents, it appears that the XAD-4 Quaternary resin has the best potential for field sampling of natural water. This resin exhibited low blank contamination and, and for the most part, was found to concentrate most neutral, acidic and semi-volatile compounds.

Breakthrough experiments should be considered for specific compounds to evaluate the effect of mass transfer due to velocity changes. Breakthrough may not occur for large volumes of water samples with trace organic contaminants due to the high capacity of the XAD-4 resin, but high concentrations of specific compounds may breakthrough.

Future research on the XAD-4 Quaternary resin for concentration of trace organics may concern:

1) Several different column dimensions to further evaluate the effect of flow rate for field sampling column size.

2) Reduction of humic substances concentration, and evaluation of the specific toxic organic compounds.

3) Experiments with known organic compounds in actual drinking water samples to evaluate the resin efficiency due to suspended matter, and soluble inorganic salts.

SECTION 4

PROJECT DESCRIPTION

In order to properly assess the risk associated with the consumption of waterborne organic substances, a method must be developed for the isolation and/or concentration of the organic substances. For methods utilizing concentration techniques, a 50-fold concentration is acceptable, but further concentration is desirable.

The fact that is is not possible to identify a large portion of the organic material present in water makes it important that the concentration/isolation procedure avoid or minimize any alteration of the original substances. Even though bacteriostats, and bactericides are routinely used to prevent bacterial contamination during the handling, processing, and storage of water samples, their effect on subsequent toxicological testing must be considered. Another factor that must be evaluated, because of its possible impact on in vivo and in vitro toxicological testing, is whether toxic inorganic substances are also isolated/concentrated by the method.

The EPA has, therefore, evaluated approaches to the concentration and/or isolation of organics from water. Twenty-two organic compounds (Table 1) were selected as being representative of the classes of compounds normally encountered in aqueous systems.

The contract, awarded to Envirodyne Engineers, Inc. (EEI), was based on the investigation of quaternized XAD-4. Several important features of the concentration/isolation technique were:

- Concentration of the 22 organic compounds not less than 50-fold
- Performance of mass balance determinations for each compound to determine whether unrecovered amounts of each substance were the result of volatilization, adsorption, chemical transformation, etc.
- Identification and quantification of contaminants introduced by the procedure through the use of appropriate blanks.
- Determination of the effect of a 2 ppm chlorine residual on blank samples taken through the isolation/concentration technique procedure, identifying any new chlorinated compounds formed.
- Evaluation of the effect of humic substances on the recovery of the other 21 organic compounds.
- Determination of the recovery of lead added as lead nitrate at a concentration of 25 ppb.

TABLE 1. ADSORPTION SYSTEM MODEL ORGANIC COMPOUNDS

Acids	Amount	Amines	Amount
Quinaldic	50	Quinoline	50
Trimesic	50	Caffeine	50
Stearic	50	5-Chlorouracil	50
Humic	2000		
Glycine	50	**Esters**	
		bis(2-ethylhexyl)phthalate	50
Carbohydrate			
Glucose	50	**Chlorobiphenyls**	
		2,4'-Dichlorobiphenyl	50
Aldehyde		2,2',5,5'-Tetrachlorobiphenyl	5
Furfural	50		
		Ketones	
Hydrocarbons			
		Isophorone	50
1-Chlorododecane	5	Anthraquinone	50
Biphenyl	50	Methyl isobutyl ketone	50
PAH		**Phenols**	
Phenanthrene	1	2,4-Dichlorophenol	50
		2,6-di-tert-butyl-4-methyl phenol	50
THM			
Chloroform	50		

Amounts in ug/l.

SECTION 5

DESCRIPTION OF EQUIPMENT AND PROCEDURES

5.1 BENCH-SCALE COLUMN AND RESIN PREPARATION

The apparatus used during bench-scale studies was modeled after work done by G. A. Junk, J. J. Richard, et al. (1). The adsorption/desorption column was 37 cm long x 1 cm I.D. In most bench-scale studies, this column was filled with 13 cm of XAD-4 Quaternary resin (OH^- form) of 40 to 80 mesh. This was equivalent to approximately 10 cm^3 of wet resin. A diagram of the apparatus used for the isolation/concentration of organics from water is shown in Figure 1. Figure 2 shows the eluant concentration apparatus designed by G. A. Junk with changes noted. Glassware shown in Figures 1 and 2 was manufactured by Southwestern Glass of St. Louis, Missouri (2).

The resin clean-up procedure used during this project utilized Soxhlet extraction with the same solvents used for elution. This assured that any impurities would be eluted prior to the actual adsorbent studies. Combining the best recommendations from previous studies, the following purification procedure was used in our laboratory.

1) A slurry of the resin was made with distilled water.

2) The resin was stirred gently.

3) The resin fines were removed by decantation.

4) Steps 1 through 3 were repeated three times.

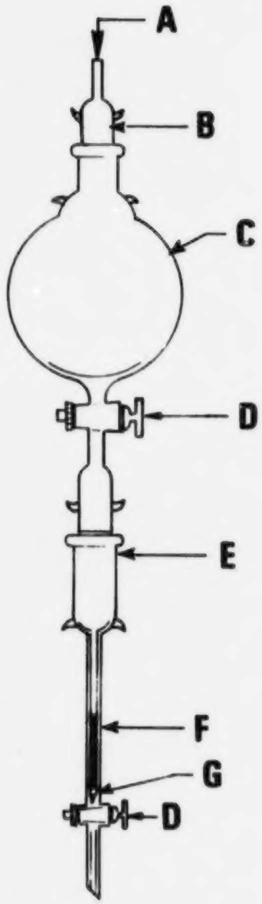
5) The resin was rinsed with methanol three times.

6) The resin was then purified by sequential solvent extractions with methanol, acetonitrile and dietheyl ether in a Soxhlet extractor for 8 hours per solvent.

7) The purified resin was stored in glass-stoppered bottles under water to maintain its purity.

8) The resin was not allowed to dry, since cracking results in the release of impurities from the interior of the resin.

One other solvent, methylene chloride, was also used for resin clean-up, but only during the resin blank study. The XAD-4 Quaternary resin was stored in the chloride form under water rather than methanol, since it was noted by our consultants (G. A. Junk and J. S. Fritz) that XAD-4 Quaternary resin is not stable when stored under methanol.



A) Pure Inert Gas Pressure Source

B) Cap

C) 2-Liter Reservoir

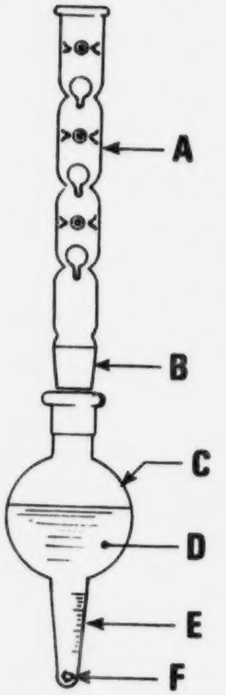
D) PTFE Stopcock

E) 24/40

F) 1.0 cm - I.D. x 37 cm Long Glass Tube Packed with 13 cm Resin

G) Silanized Glasswool Plug

Figure 1. Apparatus for extracting organic solutes from water



A) Snyder Distillation Column

B) 24/40

C) 100 ml Vessel

D) Eluant Solvent

E) Graduated and Calibrated Taper

F) Small Boiling Chip

Figure 2. Concentration aparatus

The XAD-4 Quaternary resin used in these studies was prepared by the Ames Laboratory in Ames, Iowa. This resin had been used in studies by the Ames group for the adsorption and selective separation of acidic material in wastewaters. For this study, the resin was chosen for its effectiveness in concentrating anionic material from solution. At the same time, it was thought that sufficient sites would be available to effectively adsorb neutral organic compounds from water. The resin was basically an XAD-4 macroreticular cross-linked polystyrene into which a trimethylamine group was introduced. The resin was stored in the chloride form, but converted to the hydroxide form before use in the resin sorption experiments.

The bisulfite (HSO_3) form of the XAD-4 Quaternary resin was used for the evaluation of several problem compounds and was cleaned up in the same manner as the OH^- form.

Carbonaceous resins (i.e. XE-340) were cleaned up by a somewhat different procedure, as follows:

1) The resin was extracted with methylene chloride for 24 hours in a Soxhlet extractor.

2) The resin was dried in an oven at 104°C overnight.

3) The clean resin was stored in a clean, glass-stoppered bottle.

4) Before application, the resins were hydrated by soaking in methanol for 1 hour.

5.2 SAMPLE PREPARATION

Organic free water was prepared by the passing of tap water through two deionization beds. The effluent from the second bed went through a Millipore "Super Q" system consisting of:

1) Prefilter (to remove solids)

2) Carbon filter (to remove organics)

3) Ion exchange filter (to remove organics)

4) Final filter (to remove solids)

Three inorganic salts were added during most studies (except where noted) either by dissolving appropriate amounts of solids in water or by adding appropriate volumes of concentrated salt solutions. The final salt concentrations, as required in the statement of work, were as follows (in mg/l):

1) $CaCl_2.2H_2O$ - 47

2) $CaSO_4$ - 120

3) $NaHCO_3$ - 70

The model compounds selected by EPA to evaluate the isolation procedure are shown in Table 1 and were added to the water by injecting a calibrated volume of a standard solution in acetone, methanol, diethyl ether, water, or other solvent. Table 1 also shows the concentration of each model compound as required in the statement of work.

Among the 22 model compounds, glucose, 5-chlorouracil, glycine and caffeine standards were prepared in water. Anthraquinone was prepared in dimethyl formamide. All other model compounds were prepared in acetone or methanol. Humic acid standard was prepared in 0.1N sodium hydroxide and pH was tested to be above 11.0.

In the course of the experiments, it was noted that after the addition of the salts at the specified concentrations, there was some precipitation of salt (believed to be $CaCO_3$) in the reservoir prior to passing the water through the resin. Since these particulates could have an effect on the isolation/concentration efficiency of some model compounds, it was decided to adjust the pH as a means of correcting the problem. The pH was, therefore, adjusted from 8.5 to 7.0, and this seemed to have corrected the problem. Therefore, throughout the bench-scale study, the pH was measured before the concentration/isolation step, and corrections were made if necessary.

5.3 COLUMN ADSORPTION/DESORPTION SCHEME

The XAD-4 Quaternary resin was changed from the chloride to hydroxide form by passing 75 ml of 0.1N NaOH through the column, followed by organic-free Millipore water until the pH of the effluent water was neutral (approximately 100 ml).

In a typical bench-scale study, five columns (Section 5.1) were set up under the strict quality control/quality assurance (QA/QC) requirements of this project: one column for control of reagents and glassware; one column for the control of the resin blank; and triplicate columns for model compound studies.

When the reservoir (with a one-hole connector) was filled with water, salts were added, and the compounds were spiked. pH was adjusted with 1N HCl to 7.0. The reservoir was capped and swirled for a few seconds. The upper and lower stopcocks were opened and pressure was applied using high pressure ultra-pure nitrogen gas. The flow rate was controlled by the nitrogen cylinder pressure, and by using the fine adjustment on the resin column stopcock. Two flow rates were studied and are described during the presentation of results. The initial flow rate used was 20 to 25 ml/min (120-150 B.V./hr). A lower flow rate of approximately (48 B.V./hr) was studied after breakthrough of quinaldic acid was observed.

When most of the sample had passed through the column and the liquid level was at the top of the resin, the reservoir was washed with 25 ml of water and drained through the column. The effluent water was preserved and stored in a cooler for future extraction.

In general, desorption was accomplished in the same column with series of solvents for the elution of neutral, basic and acid compounds. The following steps (or combinations of these steps) were used to desorb different classes of model compounds:

1) Six 25 ml of distilled diethyl ether. The first 25 ml portion of distilled ether was added to the resin column, and the column was agitated to free the resin. The column was then allowed to stand for 5 to 10 minutes before draining. The second through the sixth 25 ml portion of ether eluants were used for desorption by gravity flow without agitation and were combined with the first aliquot. In some experiments, additional 25 ml aliquots of ether were used to elute the column.

2) Two 25 ml methanol. Used for better desorption of caffeine and removal of any remaining water from Step 1.

3) Two 10 ml ether. Used for removal of residual methanol from Step 2 which could interfere in the methylation of acidic compounds.

4) Two 25 ml 0.1N HCl/ether. Used for removal of acidic compounds.

5) Two 25 ml 0.1N HCl/methanol. Used for removal of acidic compounds.

6) Two 25 ml saturated HCl/methanol. Used for removal of humic substances.

Saturated HCl in methanol and ether was prepared by bubbling anhydrous, electronic grade, HCl gas through three containers of each solvent in series. A caustic trap was added after the third container to neutralize the excess HCl gas. The normality of each batch was determined by titration against a known sodium hydroxide 10N solution. 0.1N HCl/ether was prepared by dilution in ether and the normality was checked by standardization against a known 0.1N sodium hydroxide solution. Fresh 0.1N HCl/ether was prepared in most cases to assure the correct normality.

One additional step (added late in the desorption scheme) consisted of rinsing the column with 0.1N HCl in water to remove lead compounds. This was necessary since lead nitrate at 25 ppb would precipitate, and lead was removed by the resin acting as a filter. This step may not be necessary in real field concentration/isolation of trace organic compounds.

5.4 DRYING AND CONCENTRATION OF ELUANTS

The residual water eluted with ether (in reservoir wash and in Step 1) is removed by freezing out the water at -20°C in a refrigerator. The concentration of eluants was performed in the concentration vessel shown in Figure 2. The ether eluant was concentrated to approximately 1 ml, but the methanol eluants had to be taken to dryness and brought back with ether for better gas chromatography using capillary column and for the removal of trace amounts of water. The acidic eluants for the analysis of the acidic compounds were also concentrated and derivatized for GC/FID analysis. Several variations of the derivatization step will be described with the difficulties encountered during the analysis of acidic compounds.

The concentration step was performed initially by K-D apparatus followed by nitrogen blowdown at room temperature. The final volume of ether was taken to approximately 0.5 ml, and was adjusted to 1 ml by rinsing the walls of the concentrator tube. The acidic ether and methanol eluants were also taken to dryness by nitrogen blowdown, but the HCl or water residual was removed by heating the concentrator tube in a water bath at 60°C.

The raw materials used in this project are listed in Table 2 and the analytical instruments used are listed in Table 3.

TABLE 2. RAW MATERIALS

Material	Source
Quinaldic Acid	Aldrich Chemical Company
Trimesic Acid	Eastman Kodak Company
Stearic Acid	Fisher-Scientific Company
Glycine Acid	Fisher-Scientific Company
Furfural	Fisher-Scientific Company
Quinoline	Eastman Kodak Company
Caffeine	Aldrich Chemical Company
5-Chlorouracil	Sigma Chemical Company
Glucose	Baker Chemical Company
2,4'-Dichlorobiphenyl	Analab, Inc.
2,2',5,5'-Tetrachlorobiphenyl	Analab, Inc.
Bis(2-ethylhexyl)phthalate	Chemical Services
1-Chlorododecane	Eastman Kodak Company
Biphenyl	Eastman Kodak Company
Isophorone	Aldrich Chemical Company
Anthraquinone	Eastman Kodak Company
Methyl isobutyl ketone	Fisher-Scientific Company
2,4-Dichlorophenol	Chemical Service
2,6-di-tert-butyl-4-methyl phenol	Poly Science Corporation
Phenanthrene	Analab, Inc.
Chloroform	Fisher-Scientific Company
Humic substances (Fluka)	EPA
n-Undecane	Analabs, Inc.
n-Pentadecane	Analabs, Inc.
XAD-4 Quaternary	Ames Laboratory
Distilled Water	Millipore Catalog No.
Methylene Chloride	Omnisolve, pesticide grade
Acetone	Omnisolve, pesticide grade
Ether	Baker Chemical Company
Methanol	Baker Chemical Company
Hydrochloric Acid	Fisher-Scientific Company
Sodium Hydroxide	Fisher-Scientific Company
Hydrochloric Acid Gas	Ace Acetylene Gas
Acetonitrile	Baker Chemical Company
Water	Millipore Super-Q System

TABLE 3. ANALYTICAL INSTRUMENTS

Instrument	Model Number	Manufacturer
Gas Chromatographs	5840A 5830A	Hewlett-Packard Hewlett-Packard
Liquid Gas Chromatograph	1084B	Hewlett-Packard
Flame Ionization Detector	-	Hewlett-Packard
Electron Capture Detector	-	Hewlett-Packard
Ultra-Violet Detector	-	Hewlett-Packard
Integrators	5840A 18850A	Hewlett-Packard Hewlett-Packard
L. C. Terminal	79850B	Hewlett-Packard
Gas Chromatograph/Mass Spectrometer	1085	Hewlett-Packard
Data System	-	Hewlett-Packard
Spectrophotometer	100	Bausch & Laumbe
Atomic Absorption	457	Instrumentation Labs
Graphite Furnace	555	Instrumentation Labs

SECTION 6

ANALYTICAL METHODS DEVELOPMENT

Certain criteria and assumptions were used in the development of analytical methods. It was assumed that one liter of water spiked with model compounds would be used in the laboratory scale experiments. It was also assumed that the extracts taken for analysis could be reduced to 1 ml prior to analysis. The objective of the analyses would be to permit measurement at all values in excess of 1 to 2% of the concentration levels specified (i.e. for those compounds specified at 50 ug/l, one should be able to detect and measure concentration in the range of 1 to 50 ug/l).

Table 4 summarizes the analytical methods used for the 22 model compounds. Several problem compounds (including acids) were analyzed by a variety of methods that are described later. Linearity curves were prepared for each compound and for every type of detector or analytical method used throughout the project.

The analytical methods shown in Table 4 were continuously modified since several resins showed different characteristics during the concentration of the model compounds. In addition, the extraction of several model compounds from the effluent water (or the analysis of the reservoir rinse) necessitated changes in the analytical methods.

In the following section, the analytical methods used for the evaluation of XAD-4 Quaternary resin are described.

For analytical purposes, the compounds were grouped as shown in Table 5.

In summary, the general desorption analytical scheme was as follows:

Ether Reservoir Rinse (2 x 20 ml distilled ether): Freeze out water at -20°C. Measure the volume of the decanted ether. Remove the following aliquots:

5 ml for 5-chlorouracil analysis (HPLC)
5 ml for quinaldic and trimesic acids (HPLC)
5 ml for quinaldic, trimesic and stearic acids
 and 5-chlorouracil (GC/FID capillary)
5 ml for humics analysis
1 ml for chloroform (GC/ECD)

Concentrate the remainder to 1.0 ml and spike with 5 ug n-Pentadecane internal standard. Analyze for all Group I compounds by capillary GC/FID (Section 6.3).

TABLE 4. ANALYTICAL METHODS FOR MODEL COMPOUNDS

Group I	Description of Methods
Methyl isobutyl ketone	GC/FID Capillary
Furfural	HPLC and GC/FID Capillary
Isophorone	HPLC and GC/FID Capillary
2,4-Dichlorophenol*	GC/FID Capillary
Quinoline	GC/FID Capillary
Biphenyl	HPLC and GC/FID Capillary
1-Chlorododecane	GC/FID Capillary and GC/Hall
2,6-di-tert-butyl-4-methyl phenol	HPLC and GC/FID Capillary
2,4'-Dichlorobiphenyl	GC/FID Capillary, GC/ECD, GC/Hall
Phenanthrene	HPLC and GC/FID Capillary
Caffeine	HPLC and GC/FID Capillary
2,2',-5,5'-Tetrachlorobiphenyl	GC/FID Capillary, GC/ECD, GC/Hall
Anthraquinone	HPLC and GC/FID Capillary
Bis(2-ethylhexyl)phthalate	HPLC and GC/FID Capillary
Group II	
5-Chlorouracil	HPLC
Stearic acid	Diazomethane derivatization, GC/FID Capillary
Quinaldic acid	Diazomethane derivatization, HPLC Diazomethane derivatization, GC/FID Capillary Direct aqueous injection, HPLC (paired ion)
Trimesic acid	Diazomethane derivatization, HPLC Diazomethane derivatization, GC/FID Capillary Direct aqueous injection, HPLC (paired ion)
2,4-Dichlorophenol*	GC/FID Capillary
Humic Substances	UV-visible spectroscopy
Group III	
Glucose	Derivatization, GC/FID or spectrophotometric
Glycine	TAB derivatization, GC/FID, fluorometry
Group IV	
Chloroform	GC/ECD

*2,4-Dichlorophenol appears in both Groups I and II.

TABLE 5. ANALYTICAL PROCEDURES

Group I	mg/l	Reference - Analytical Procedure (Section No.)
Methyl isobutyl ketone	50	6.3
Furfural	50	6.3
Isophorone	50	6.3
2,4-Dichlorophenol*	50	6.3
Quinoline	50	6.3
Biphenyl	50	6.3
1-Chlorododecane	5	6.3
2,6-di-tert-butyl-4-methyl phenol	50	6.3
2,4'-Dichlorobiphenyl	50	6.3
Phenanthrene	1	6.3
Caffeine	50	6.3
2,2',-5,5'-Tetrachlorobiphenyl	5	6.3
Anthraquinone	50	6.3
Bis(2-ethylhexyl)phthalate	50	6.3
Group II		
5-Chlorouracil	50	6.5
Stearic acid	50	6.3
Quinaldic acid	50	6.4
Trimesic acid	50	6.4
2,4-Dichlorophenol*	50	6.3
Humic Substances	2000	6.7
Group III		
Glucose	50	6.2
Glycine	50	6.1
Group IV		
Chloroform	50	6.6

*2,4-Dichlorophenol appears in both Groups I and II.

Ether Eluent (6 x 25 ml): Freeze out water. Measure the volume and remove 1 ml for analysis of chloroform. Concentrate the remainder to 1 ml and spike with 10 ug of n-Pentadecane internal standard. Analyze for all Group I compounds by capillary GC/FID (Section 6.3).

Methanol Eluent (2 x 25 ml): Measure the volume and remove 5 ml for humics analyses. Concentrate the remainder to dryness and solvent exchange to methylene chloride to a final volume of 1.0 ml; spike with 20 ug of internal standard. Analyze this fraction by GC/FID capillary for all Group I compounds with special emphasis on caffeine.

0.1N HCl/Ether (2 x 25 ml): Measure the volume and analyze as 0.1N HCl/Methanol.

0.1N HCl/Methanol (2 x 25 ml): Measure the volume and remove aliquots for the following analyses:

5-chlorouracil (Section 6.5)
Quinaldic and trimesic acids (Section 6.4)
Humic substances (Section 6.7)
2,4-dichlorophenol (Section 6.3) (after dilution with water, 2,4-dichlorophenol in acid form was extracted with 3 x 25 ml of CH_2CL_2, then concentrated to 1.0 ml and 20 ug of n-Undecane internal standard was added prior to gas chromatographic determination)

Concentrate the remaining volume to near dryness by nitrogen blowdown at room temperature. Add several milliliters of distilled ether, concentrate to near dryness in a water bath, and repeat four or five more times to remove HCl (Section 5.4). Esterify with diazomethane (3) and analyze by capillary GC/FID for stearic acid and 2,4-dichlorophenol (5-chlorouracil also gave a derivative with diazomethane). Retain all concentrate after GC/FID analysis for possible HPLC analysis.

Saturated HCl/Methanol: Measure the volume of eluant and analyze spectrophotometrically for humic substances (Section 6.7).

Effluent Waters: Measure the volume of water, remove 1 ml for GC/ECD analysis of chloroform (Section 6.6). Adjust the pH of the remaining water to >11, extract with 3 x 100 ml CH_2Cl_2; adjust the pH to <2, extract with 3x 100 ml CH_2Cl_2. Concentrate the CH_2Cl_2 extracts separately to a final volume of 1.0 ml; spike with 5 ug of n-Pentadecane and n-Undecane internal standard. Analyze the basic extract for all Group I compounds by capillary GC/FID (Section 6.3). Analyze the acidic fraction for stearic acid after methylation and 2,4-dichlorophenol by capillary GC/FID (Section 6.3)

6.1 ANALYSIS OF GLYCINE

In order to study the characteristics of XAD-4 Quaternary resin on glycine at 5 ppb, it was decided to evaluate a fluorometric procedure for glycine as reported in the literature. This method consists of measurement by fluorometry of the fluorescamine derivative of glycine. Calibration standards of 0, 15, 20, 25, 30, 35, 40, 45, and 50 ppb were prepared and the responses (Turner Model 111 Fluorometer; No. 8-60, 365 nm primary filter and No. 4, 465 nm secondary filter) of these standards gave a linear plot vs. concentration. The method was found to be both sufficiently accurate and sensitive for use on this project. An anticipated difficulty in its use, however, is that other model compounds might fluoresce under the same conditions and cause inteference in the measurement of glycine in the presence of other model compounds. Therefore, other model compounds were included in reagent blanks to determine their effect. A possible solution to that problem involves the use of HPLC for separation, followed by fluorescence detection. This was not possible since we did not have this detector on our HPLC instrument.

6.2 ANALYSIS OF GLUCOSE

Glucose derivatization techniques did not prove to be successful at low or high concentrations. Therefore, for the preliminary evaluation of glucose behavior on XAD-4 Quaternary resin (OH^-), it was decided to use higher concentrations and to analyze by a colorimetric procedure. The following procedure was used.

Five ml of solution was pipetted into a 12.5 ml vial, and 2.5 ml of copper sulfate solution was added. The vial was then sealed with a septum and heated in a boiling water bath for 30 minutes. The vials were then allowed to come to room temperature. One ml of arsenomolybdate solution was added and the green color allowed to develop for 2 minutes. The absorbance at 620 nm was then read on a spectrophotometer (4).

Derivatization techniques for the analysis of glucose at 50 ppb in water are listed below:

1) Phenly osazone (LC) reference: Shiner, Fuson and Curtin, "The Systematic Identification of Organic Compounds," 5th edition, Wiley & Sons, pp. 147-149, 1964.

2) 2,4-dinitrophenyl hydrazone (LC) reference: Ibid

3) Trimethylsilane (TMS) (GC) reference: Pierce Chemical Company Handbook and General Catalog, Silylation Methods Nos. 10 and 20, pp. 176-182, 1979-1980.

As stated previously, the difficulties associated with the above techniques have been primarily due to the low levels of glucose and the presence of water. In a meeting with EPA staff members, it was suggested to preserve the effluent water samples and send them to the EPA's laboratory for the analysis of glucose. This idea was suggested in order to obtain a mass balance for the pilot plant study. Only the effluent water samples were analyzed since it appeared tha the XAD-4 Quaternary resin in OH^- or HSO_3^- would not concentrate glucose.

6.3 ANALYSIS OF GROUP I MODEL COMPOUNDS BY CAPILLARY GC/FID

Capillary gas chromatography using a flame ionization detector was pursued from the beginning of this project. A 17 meter glass capillary column coated with OV-101 was initially used, but in order to improve performance with respect to thermal stability, inertness and column polarity, a 60 meter fused silica column was purchased for use in both GC/FID and GC/MS analysis. The 60-meter column was coated with a non-extractable bonded phase (DB-5) which is equivalent to SE-54. GC conditions are listed in Appendix A. This column was divided into two 30 meter columns.

Methods development work was also performed using GC/MS. In order to help confirm the analysis of compounds of interest, a mass spectral library of the compounds (or their derivatives which will be used for analysis) was compiled using mass spectra from the Wiley Library, available from our instrument, or from actual runs using standard compounds. GC/MS was used in the studies primarily to identify artifacts from blank resin experiments and to confirm the identification of model compounds in actual runs.

The 14 model compounds are: 1-chlorododecane, biphenyl, phenanthrene, bis(2-ethylhexyl)phthalate (BEHP), anthraquinone, 2,6-di-tert-butyl-4-methylphenol (BHT), 2,2',5,5'-tetrachlorobiphenyl, 2,4'-dichlorobiphenyl, furfural, quinoline, caffeine, isophorone, methyl isobutyl ketone, and 2,4-dichlorophenol.

Relative response factors were developed to permit the use of internal standardization in the capillary gas chromatographic analyses of 14 model compounds. This internal standardization procedure used n-Pentadecane and n-Undecane as internal standards and was proposed for use only in the final stage of analysis (i.e. internal standard is added after concentration of extract and prior to gas chromatographic analysis). The internal standardization procedure was intended to reduce error due to measurement of final extract volume, volume injected, and variations in responses of samples and standards. It did not, however, compensate for any losses occurring due to extraction and concentration.

The above listed 14 model compounds were studied to determine their relative response factors. The relative response factors of phenanthrene and caffeine checked out closely with values determined earlier. Table 6 presents a summary of these determinations. From the above list of compounds, HPLC could also be used to analyze eight compounds, but a time program for wavelength is required for this capability (see Table 7 and Appendix B for LC conditions).

6.4 ANALYSIS OF QUINALDIC AND TRIMESIC ACIDS BY HPLC

Due to derivatization problems of quinaldic and trimesic acids at 5 ppb concentration levels, an HPLC method was evaluated using an ion pairing technique. Ion pairing/HPLC at low concentration levels was not satisfactory due to either the presence of salts, the neutralization step, or solvent incompatibility. Many experiments on XAD-4 Quaternary resin were performed and some results indicated recoveries for trimesic acids, but an interferring peak generally caused inconsistent results for quinaldic acid.

Since it was known that the XAD-4 Quaternary resin can concentrate the acidic compounds by an anionic exchange process, the ion pairing/HPLC method was evaluated at 5 to 50 ppm concentration levels. Standard solutions were prepared in water, 0.1N HCl/ether, and 0.1N HCl/methanol. HPLC conditions are shown in Appendix C.

The method proved satisfactory for both quinaldic and trimesic acids, and was thus utilized in the experiment to evaluate the concentration of acidic model compounds on the XAD-4 anionic resin.

The methylation of quinaldic, trimesic and stearic acids was probably inconsistent due to the presence of water, HCl or background oily material from the resin. This was proven on many occasions when 0.1N HCl/ether or 0.1N HCl/methanol fractions were concentrated to 1.0 ml (or dryness) prior to the addition of diazomethane, but the same esterification technique was evaluated at high concentrations of the acidic compounds, and 5-chlorouracil. This was pursued because of a 500 fold concentration for the 500 liter pilot plant study. The GC conditions for the analysis of quinaldic, trimesic and stearic acids, and 5-chlorouracil methyl esters, were the same as those for the other 14 model compounds with capillary FID (Section 6.3). Table 8 shows the response factors of the above four acidic compounds (0.1N HCl/ether and 0.1N HCl/methanol).

6.5 ANALYSIS OF 5-CHLOROURACIL BY HPLC

The purpose of this evaluation was to demonstrate that 5-chlorouracil could be determined in 0.1N HCl/methanol, prior to analysis of these eluants on actual samples. Standards were also prepared in water and in methanol, in order to determine whether the HCl has any effect on the analysis. HPLC conditions are shown in Appendix D.

TABLE 6. INTERNAL STANDARDIZATION FOR 14 MODEL COMPOUNDS BY GC/FID CAPILLARY ANALYSIS

Model Compounds	Response Factors at Indicated Concentrations of Model Compounds (ppm)				
	1	5	10	20	40
n-Undecane Internal Standard:					
Methyl isobutyl ketone	1.94	2.07	1.76	1.73	1.83
Furfural	3.08	2.65	2.48	2.36	2.15
Isophorone	1.47	1.32	1.28	1.26	1.22
2,4-Dichlorophenol	5.35	3.36	2.98	2.74	2.45
Quinoline	1.44	1.28	1.24	1.21	1.14
Biphenyl	0.99	0.95	0.93	0.92	0.87
1-Chlorododecane	1.39	1.29	1.23	1.23	1.20
n-Pentadecane Internal Standard:					
2,6-di-tert-butyl-4-methyl phenol	1.27	1.19	1.19	1.20	1.22
2,4'-Dichlorobiphenyl	1.35	1.24	1.12	1.21	1.16
Phenanthrene	0.87	0.85	0.82	0.84	0.78
Caffeine	3.47	3.11	2.84	2.77	2.48
2,2',-5,5'-Tetrachlorobiphenyl	1.61	1.61	1.54	1.57	1.44
Anthraquinone	1.44	1.35	1.27	1.28	1.10
Bis(2-ethylhexyl)phthalate	1.91	1.58	1.40	1.38	1.18

Internal Standard concentration = 5 ppm (5 ug/ml)

TABLE 7. ANALYSIS OF EIGHT MODEL COMPOUNDS BY HPLC IN GROUP I

	Concentration (ug/ml)	RT (ug/ml)
Isophorone	13.95	2.98
Anthraquinone	6.90	5.33
Biphenyl	12.55	7.16
2,4'-Dichlorobiphenyl	10.10	10.43
2,6-di-tert-butyl-4-methyl phenol	17.40	11.99
2,2',-5,5'-Tetrachlorobiphenyl	4.30	12.95
Bis(2-ethylhexyl)phthalate	16.70	20.41

TABLE 8. RESPONSE FACTORS AT INDICATED CONCENTRATIONS OF FOUR MODEL COMPOUNDS BY GC/FID CAPILLARY ANALYSIS (SECTION 6.3)

Internal Standard Concentration = 20 ppm n-pentadecane

Compound	25 ppm	50 ppm	100 ppm	200 ppm**
0.1N HCl/Ether*:				
5-Chlorouracil	7.48	8.23	8.19	5.89
Quinaldic acid	1.57	2.04	1.90	1.08
Trimesic acid	3.32	3.63	3.23	2.77
Stearic acid	2.35	2.20	2.02	1.84
0.1N HCl/Methanol*:				
5-Chlorouracil	6.88	4.94	6.09	5.54
Quinaldic acid	1.20	1.05	1.07	1.01
Trimesic acid	2.57	2.40	2.35	2.30
Stearic acid	1.73	1.56	1.48	1.44

*Four model compounds can be analyzed in HCl/Ether or HCl/Methanol by diazomethane methylation at 25-100 ppm.

**Response factors are generally lower at 200 ppm and, therefore, should not be used.

Standards prepared in water and in 0.1N HCl/methanol proved satisfactory, while the methanol standards gave a double peak and were not satisfactory.

The standards in 0.1N HCl/methanol were prepared by adding 2.0 mls of acidic solvent to a 10 ml volumetric flask, neutralizing with 2N NH_4OH and 1N HCl, and bringing to volume with water.

6.6 ANALYSIS OF CHLOROFORM

Chloroform was analyzed by direct injection of the ether eluant prior to concentration and by liquid-liquid extraction of the effluent resin column. This method was taken from the Federal Register (Volume 44, No. 231, November 29, 1979 for the analysis of "Trihalomethanes in Drinking Water - Part II"). The chromatographic conditions are shown in Appendix E.

This method proved satisfactory, with the exception of background contamination of chloroform which required correction.

6.7 ANALYSIS OF HUMIC SUBSTANCES

The humic substances (Fluka) supplied by the EPA were studied for solubility in methanol, acetone, ether, and water at various pH values.

Stock solutions of humic substances were prepared in water at a pH of 11. Linearity curves were developed by using a colorimeter at 330 and 345 nm. Since a mass balance was required for the humic substances, the linearity curves were prepared in water, 0.1N HCl/ether, 0.1N HCl/methanol, and saturated HCl/methanol. It is important to note that the normality of the acid or the solvent type did not significantly affect absorption. Therefore, for the pilot plant study, only the 0.1N HCl/methanol curve was used for the analysis of humics.

6.8 ANALYSIS OF CHLORINE AND CHLORINATED FORMING COMPOUNDS

The effect of chlorine on the separation/concentration of the XAD-4 Quaternary resin was studied by adding calcium hypochlorite to organic free water at 2 ppm residual chlorine concentration.

Chlorine and chlorinated forming compounds were analyzed in the following fractions:

1) Residual chlorine in the effluent water by the iodimetric method (5)

2) Ether eluant was analyzed by GC/MS, under the conditions listed in Appendix F.

3) GC/ECD analysis of the effluent water using the same procedure outlined in the analysis of chloroform (Section 6.6).

4) GC/EC analysis of the effluent water using pentane liquid/liquid extraction, followed by injection with the chromatographic conditions listed in Appendix G.

6.9 ANALYSIS OF LEAD BY ATOMIC ABSORPTION

The graphite furnace atomic absorption (A.A.) method was used to analyze the resin column effluent water sample. The following A.A. conditions were used:

Wavelength	283.3 nm
Lamp Current	5 m.a.
Slit Width	0.5 nm
Drying Time & Temperature	30 Sec - 125°C
Ashing Time & Temperature	30 Sec - 500°C
Atomization Time & Temperature	30 Sec - 2700°C
Purge Gas Atmosphere	Argon

6.10 ANALYSIS OF STEARIC ACID

A packed column was used to analyze stearic acid after methylation with diazomethane. The chromatographic conditions are listed in Appendix H.

SECTION 7

RESULTS AND DISCUSSION

7.1 QA OBJECTIVES FOR MEASUREMENT DATA IN TERMS OF PRECISION, ACCURACY, COMPLETENESS, REPRESENTATIVENESS AND COMPARABILITY

The quality assurance objectives of this project were derived from and based on the requirement that mass balance determinations be performed for each of the model compound using the proposed method. The project had an advantage over some environmental measurement programs in that the true values (corresponding to the amount of each compound added) were known, and the different fractions analyzed for mass balance purposes totaled the original amount added. The amount of compound(s) "unaccounted for" thus provided an indication of the quality of the work performed in isolating, concentrating and analyzing in each experiment.

To determine mass balances, three samples were analyzed from each sorbent experiment; eluants from the sorbent, aqueous effluent, and reservoir rinse. Certain compounds were left on the resin (i.e. not desorbed) or lost to the atmosphere by volatility. Most compounds, however, desorbed readily and precaution was taken to avoid losses due to volatility. The accurate analyses of the three samples mentioned previously were adequate to determine mass balances.

7.2 EXTRACTION OF MODEL COMPOUNDS

The mass balance studies required that analyses be made of the aqueous effluent and reservoir, as well as the organic eluant from the resin. Studies analyzing aqueous effluents were only performed to provide preliminary resin evaluation.

In order to analyze the aqueous solutions, it was usually necessary to extract the model compound using an organic solvent. Therefore, studies were performed to determine the extraction efficiencies of model compounds from water using methylene chloride. The results of these studies are summarized in Table 9. All experiments were performed using 50 ug of the compounds tested in 1 liter of water.

Chloroform was omitted from the extraction studies since our laboratory was experienced in its analysis by liquid/liquid extraction with hexane as well as the purge and trap method.

From Table 9 it can be seen that not all compounds were efficiently extracted from aqueous solution. In fact, several compounds were not recovered at all. The reasons for these low recoveries vary from one compound to another. Quinaldic and trimesic acids appear to

TABLE 9. EXTRACTION EFFICIENCIES OF MODEL COMPOUNDS FROM WATER USING METHYLENE CHLORIDE

Compounds	Average Percent Recovery of 3 Determinations	Extraction/Analytical Method
Anthraquinone	86.6	Extraction with 3 x 100 ml CH_2Cl_2 Solvent exchange to acetonitrile Analysis by HPLC/UV (Section 6.3)
2,4-Dichlorobiphenyl	93.3	Extraction with 3 x 100 ml CH_2Cl_2 Solvent exchange to hexane Analysis by GC/ECD (Section 6.8)
2,2',5,5'-Tetrachlorobiphenyl	85.0	
bis(2-Ethylhexyl)phthalate	82.5*	Extraction with 3 x 100 ml CH_2Cl_2 Analysis by GC/FID (Section 6.3)
1-Chlorododecane	72.3	
Biphenyl	76.2	
2,4-Dichlorophenol (pH <2)	92.9	
2,6-di-tert-Butyl-4 methylphenol (pH <2)	66.2	
Quinaldic Acid (pH <2)	0	Extraction with 3 x 100 ml CH_2Cl_2 Derivatize with CH_2N_2 Solvent exchange to acetonitrile Analysis by HPLC/UV (Section 6.4)
Trimesic Acid (pH <2)	0	
Stearic Acid	93.5	Extraction with 3 x 100 ml CH_2Cl_2 Derivatize with CH_2N_2 Solvent exchange to hexane Analysis by GC/FID (Section 6.3)
Quinoline	73.6*	Extraction with 3 x 100 ml CH_2Cl_2 Solvent exchange to hexane Analysis by GC/FID (Section 6.3)

(Continued)

TABLE 9. (Continued)

Compounds	Average Percent Recovery of 3 Determinations	Extraction/Analytical Method
Methyl isobutyl ketone	0	Extraction with 3 x 100 ml CH_2Cl_2 Solvent exchange to hexane Analysis by GC/FID (Section 6.3)
Furfural	53.6	Extraction with 3 x 100 ml CH_2Cl_2 Solvent exchange to acetonitrile Analysis by HPLC/UV (Section 6.3)
Caffeine	0	
5-Chlorouracil	72.3	
Isophorone	61.0	
Glycine	0*	Extraction with 3 x 100 ml ethyl acetate. Derivatization Analysis by GC (Section 6.1)
Phenanthrene	78.8	Extraction with 3 x 100 ml CH_2Cl_2 Solvent exchange to acetonitrile Analysis by HPLC/UV (Section 6.3)

NOTE: *Values reported represent, with the exception of glycine, the average of triplicate extractions in each experiment. All extractions were done on water to which salts had been added as required by the project. In the case of glycine, only a single extraction was performed, and six extractions were performed for BEHP, 1-chlorododecane, biphenyl and quinoline.

be too water soluble; not even pH adjustment could improve recovery. Furfural and caffeine are also very hydrophilic compounds and do not extract with methylene chloride. Methyl isobutyl ketone, on the other hand, probably extracts well but is lost during the solvent concentration step.

Glycine was studied separately by adding this compound to water (with added salts) at a concentration of 2,000 ug/l and extracting with 3 x 100 ml of ethyl acetate. Glycine was not extracted.

As a result of these studies, it was concluded that preliminary resin evaluations by extraction of the water followed by concentration and analysis were difficult for some model compounds at the concentration levels specified for the project. Options considered for preliminary resin evaluation included increasing concentration levels to facilitate direct analysis of aqueous solutions or analysis of the organic solvent used to elute the model compound from the resin. Work was performed on methods to extract and analyze low levels of all model compounds in water in order to meet the mass balance requirements of the project. The analytical work was directed towards developing methods capable of permitting mass balances when performing pilot level (500 liters) experiments. Preliminary experiments were performed with the objective of determining sorption performance, but this did not always include complete mass balance determinations.

Extraction Efficiency for Caffeine, Trimesic Acid and Quinaldic Acid

Initial work on the extraction efficiency of caffeine indicated that methylene chloride did not extract it from water (Table 9). However, as analytical capability improved, this initial determination was put in doubt. It was decided to repeat this determination of extraction efficiency using capillary GC-FID, an internal standardization, in the analysis.

Extraction was performed using 3 x 100 ml portions of CH_2CL_2 at pH 10 and pH 4 to extract 50 ug of caffeine from 1 liter of water containing salts as required by the project. The extracts were dried over Na_2SO_4 and concentrated by K-D.

The straight chain hydrocarbon (n-pentadecane) was used as an internal standard, giving a response factor of 2.46. Results for the extraction were as follows.

Percent Extracted at pH 10	Percent Extracted at pH 4
54.9	53.7
72.6	
59.2	

Average = 62.2

The reagent blank for this experiement did not show any peak corresponding to caffeine. The results for extraction efficiency agree well with the value of 62.8% obtained when a single extraction was performed.

Extraction of trimesic and quinaldic acids from water was also evaluated by an ion-pairing procedure. Tetra-n-butyl ammonium phosphate (PIC-A, Waters Associates) was used as the alkyl ammonium counterion. This was based on a procedure reported by P. A. Realini (6). Unfortunately, the attempt was unsuccessful.

7.3 RESIN BLANK ARTIFACTS/EFFECT OF 2 PPM RESIDUAL CHLORINE

Two basic types of blank experiments were performed. One for the purpose of identifying any artifacts caused by the presence of 2 ppm chlorine to blank water used in the separation/concentration procedure, and the other for identifying any artifacts in the general resin procedure.

Blank Experiment with Chlorine

This experiment was designed to provide information regarding the effect of chlorine on the production of new chlorinated compounds. Duplicate blank experiments for both pure water and pure water spiked with 2 ppm chlorine residual were performed by the normal resin separation/concentration procedure. This was done for comparative purposes, since only compounds identified in the extract of the chlorine spiked water which are not present in the normal extract from pure blank water can be considered as true artifacts caused by the chlorine. In addition, a reagent blank was also concentrated and analyzed. The reagent blank was performed in a manner identical to the pure water blanks, except that no resin was included in the procedure. This reagent blank gave an indication of contaminants arising from sources other than the resin (i.e. glassware, water, solvents, etc.).

This experiment was performed on XAD-4 Quaternary resin in the OH^- form, and desorption was by diethylether only (i.e. HCl saturated ether not used). Calcium hypochlorite [$Ca(OCl)_2$] was used to provide the required 2 ppm chlorine concentration. Millipore Super-Q water was salted according to the general procedure and passed over a 10 ml bed volume of resin (approximate dry weight = 6 grams) at 150 B.V./hr. The resins were blown with nitrogen (3 psig) for 10 seconds to remove residual water and eluted with 3 x 50 ml portions of diethylether (peroxide formation suppressed by addition of 2% v/v ethanol).

The ether was concentrated by K-D evaporation and then solvent exchanged to hexane to give a final volume of 0.3 to 0.4 ml. In order to quantify the compounds present, the samples were spiked with a known amount of D_{10}-anthracene as internal standard just prior to injection. The concentrated extracts were analyzed by capillary GC/MS (Section 6.8).

The results of these analyses are summarized in Table 10. Note that the estimated amounts of each compound are given in terms of micrograms per gram of dry resin. In a normal resin separation/concentration procedure, these amounts would be the same, independent of the amount of water passed through the resin. Note also that some peaks could not be identified.

Waters spiked with chlorine were also analyzed after passage through the resin and showed no chlorine residual.

The blanks run in this experiment were also analyzed by GC-ECD using the same analytical conditions as those routinely used for chloroform determination (i.e. extraction method as per EPA drinking water regulations). This was done to provide for more sensitive detection of any new chlorinated compounds that might have been formed. In all five cases (i.e. two chlorine blanks, two resin blanks and reagent blank), a very large amount of chloroform and/or methylene chloride was seen in most cases above the linear range of the ECD (at 10-12 amp/mV). Methylene chloride is used daily in our laboratory as an extracting solvent.

Finally, the blanks were analyzed by GC-ECD under conditions suitable for chlorinated biphenyl analysis (Section 6.8). The same peaks (approximately 10 to 12) were seen in the two chlorine and two resin blanks. Only two to three early eluting peaks were seen in the reagent blank.

Data from this experiment has yielded the following conclusions.

1) Ethyl acetate was present in large amounts in each type of resin blank.

2) Trace amounts of other organic compounds were found in each type of resin blank.

3) Compounds identified in the chlorine blanks were also found in resin and reagent blanks.

4) No new chlorine containing compounds were identified as having originated from the addition of chlorine to the blank water.

5) Many of the compounds identified appear to have their origin as trace components of the solvents used.

6) None of the alkyl substituted aromatics identified as artifact contaminants from XAD-2 resin by EPA/Batelle were identified in this experiment.

TABLE 10. RESULTS OF BLANK EXPERIMENTS WITH CHLORINE

Peak No.	Compound	Approximate Retention Time	Concentration ug/g Dry Resin
Reagent Blank			
1	Acetic Acid	3.9	0.7
2	NI*	5.0	0.5
3	NI	5.1	0.3
4	Ethyl acetate	6.4	54.7
5	NI	7.8	0.5
6	NI	10.4	0.3
7	NI	11.3	0.7
8	Methyl palmitate	19.2	1.8
9	Methyl oleate	20.5	5.8
10	NI	20.8	1.1
11	NI	21.8	0.4
12	BEHP	23.2	0.7
13	Farnesol	25.5	1.0
Resin Blank A - Spiked Chlorine (2 ppm)			
1	Acetic acid	3.9	0.4
2	NI	4.3	0.5
3	Ethyl acetate	6.4	30.3
4	NI	7.7	0.3
5	NI	10.2	0.2
6	NI	11.0 - 11.4	1.0
7	Impurity from Internal Standard	17.5	--
8	Impurity from Internal Standard	18.1	--
9	Diisobutyl phthalate	18.9	0.1
10	Dibutyl phthalate	19.6	0.4
11	BEHP	23.3	0.2
12	Farnesol	25.5	1.2
Resin Blank B - Spiked with Chlorine (2 ppm)			
1	Acetic acid	3.9	0.5
2	NI	4.2	0.5
3	Ethyl acetate	6.3	27.3
4	NI*	7.6	0.2
5	NI	10.1	0.2
6	NI	11.0 - 11.3	0.6
7	Ethyl benzoate	12.3	0.1
10	Diisobutyl phthalate	18.8	0.2
11	Dibutyl phthalate	19.5	0.1
12	BEHP	23.3	0.2
13	Farnesol	25.6	1.2

(Continued)

TABLE 10. (Continued)

Peak No.	Compound	Approximate Retention Time	Concentration ug/g Dry Resin
Resin Blank C - Regular Blank			
1	Acetic Acid	3.9	0.5
2	NI	4.2	0.5
3	NI	5.0	0.1
4	Ethyl acetate	6.3	29.3
5	NI	7.6	0.2
6	NI	11.0	0.1
7	NI	11.2	0.6
8	Ethyl benzoate	12.2	0.1
	Diethyl phthalate	16.7	0.1
11	Diisobutyl phthalate	18.9	0.1
12	Dibutyl phthalate	19.5	0.1
13	BEHP	23.2	0.1
14	Farnesol	25.6	1.4
Resin Blank D - Regular Blank			
	Acetic Acid	Missed due to solvent vent	
1	NI	5.0	0.5
2	Ethyl acetate	6.6	27.8
3	NI	11.2	1.0
4	Impurity from Internal Standards	17.6	--
5	Impurity from Internal Standards	18.1	--
6	Dibutyl phthalate	19.0	0.1
7	BEHP	23.1	0.4
8	Farnesol	25.5	1.7

NOTE: *NI = Not identified

Clean Water Blank Experiment

This experiment was performed for the purpose of identifying any artifacts that might arise from the resin in the course of normal resin experiments. Four replicate resin blanks were run by the normal resin separation/concentration procedure. A single reagent blank was also run as part of quality control. Resin blanks and reagent blanks were run as described previously in the chlorine blank experiment, except that the final volume of concentrate was 0.100 ml.

The raw data from this experiment are summarized in Table 11.

The following summary conclusions are offered.

1) Ethyl acetate was found in all resin blanks as well as the reagent blank.

2) Trace concentrations of other organic compounds were also found in all resin blanks ranging from three compounds in Blank 2 to ten compounds in Blank 4.

3) The reagent blank was found to contain only two compounds, in contrast to the reagent blank in the previous experiment where 13 compounds were found.

These blank investigations have not indicated the XAD-4 Quaternary resin to be a significant source of artifacts, in contrast with work performed by EPA/HERL which demonstrated that the XAD-2 resin is the source of a large number of organic artifacts. The reasons for this striking difference appear to be the: 1) manner in which resin is stored, 2) order of use of elution solvents, and 3) structural differences of the resins.

Recently published work in England (7) on the XAD-2 resin indicates that the common procedure of storing the resin in methanol, and rinsing the resin in the column with water results in the resin being fractured and artifacts being released from the interior of the resin beads. By rinsing the resin with diethyl ether prior to passage of water, the fracturing of the resin and consequent release of artifacts could be avoided. In the case of the XAD-4 Quaternary resin, it is necessary to store it under water in the chloride form. This is based on information from John Richard of the Ames Laboratory, who indicated that this resin has been found to be unstable when stored in methanol. Thus, the problem of transition from methanol to water did not arise in our research, and is a reasonable explanation for the apparent absence of artifacts originating from the resin in our blank experiments.

The blank experiments have, however, indicated that the ether solvent contributed to the presence of artifacts in the blanks. The source of these artifacts has been identified in another British Publication (8). According to this report..."Diethyl ether is one solvent which has presented some problems because of peroxide formation. Combined gas-liquid chromatography and mass spectrometry

TABLE 11. RESULTS OF CLEAN WATER BLANK EXPERIMENT

Peak No.	Compound	Approximate Retention Time	Concentration ug/g Dry Resin
Reagent Blank			
1	Methyl cyclohexane	3.6	0.8
2	Ethyl acetate	5.8	10.8
Resin Blank 1			
1	Methyl cyclohexane	3.6	0.8
2	3-hexanone	5.0	0.6
3	MIBK	5.1	0.9
4	Ethyl acetate	5.7	3.8
5	NI*	6.1	4.8
6	Ethyl benzene	6.6	0.7
7	NI	11.2	2.5
8	1,2,4-trichlorobenzene	12.4	0.8
9	Diethyl phthalate	16.7	0.4
10	NI	17.5	0.5
Resin Blank 2			
1	Ethyl acetate	5.6	12.2
2	NI	6.1	4.5
3	NI	11.2	2.0
4	Diethyl phthalate	16.7	0.6
Resin Blank 3			
1	Methyl cyclohexane	3.6	0.9
2	1,1-diethoxyethane	3.9	0.6
3	3-hexanone	4.9	0.5
4	MIBK	5.0	0.5
5	2,4-dimethylhexane	5.4	5.3
6	Ethyl acetate	5.6	0.4
7	NI	6.0	3.3
8	Ethyl benzene	6.7	0.5
9	NI	9.5	0.3
10	NI	10.7	0.6
11	NI	11.2	2.5
Resin Blank 4			
1	Methyl cyclohexane	3.6	0.4
2	Toluene	4.5	0.2
3	3-hexanone	4.9	0.3
4	MIBK	5.0	0.4
5	Ethyl acetate	5.6	2.5

(Continued)

TABLE 11. (Continued)

Peak No.	Compound	Approximate Retention Time	Concentration ug/g Dry Resin
Resin Blank 4 - FRXN 16504 (continued)			
6	NI*	6.0	1.0
7	NI	9.4	1.6
8	NI	11.1	0.3
9	1,2,4-trichlorobenzene	12.4	1.0
10	NI	16.0	0.9
11	Diethyl phthalate	16.7	0.2

*NI = Not Identified

(GLC/MS) separations have shown several peaks on the GLC trace containing ethyl acetate fragments. These presumably originate from various peroxides which are decomposing at different temperatures on the column. The peroxides take part in esterificatin reactions during the course of an extraction. This is indicated by the isolation of ethyl stearate, oleate and myristate rather than the parent acid after a continuous extraction with ether. This phenomenon is particularly prevalent during extraction from acid media."

Based on these British experiments and our own work, it would appear that the following conclusions are warranted. First, the present procedure of resin storage, column preparation, passage of water sample, and solvent extraction results in negligible artifact contribution from the resin itself. Second, by reducing or eliminating peroxides as well as the 2% added ethanol, it should be possible to eliminate the presence of ethyl acetate and other esters in blanks. Thus, this project included the distillation of commercial diethyl ether immediately prior to use. In the event diethyl ether was stored, clean copper oxide ware was added to the distillation pot in order to avoid the formation of peroxides, and the ether was stored in the dark.

The above experiments were performed to evaluate the presence of artifacts in both resin blanks and reagent blanks, as well as to evaluate the effect of chlorine on the XAD-4 Quaternary resin.

Following these initial blank experiments, the laboratory began to distill the ether prior to use and store with copper wire to avoid the presence and formation of peroxides commonly present in ether as impurities. It was thus judged appropriate to repeat the resin blank experiments to determine whether the use of freshly distilled ether gave the expected improvement. It was also planned to evaluate the acidic ether and acidic methanol eluants for artifacts, which was not done in the initial blank experiments.

The following procedure was used in the recent experiment to evaluate resin and reagent blanks.

A new batch of anionic XAD-4 Quaternary resin was cleaned as follows:

1) The resin was slurried with pure (deionized) water.

2) The resin was stirred gently.

3) Resin fines were removed by decantation.

4) Steps 1 through 3 were repeated three times.

5) The resin slurry was transferred to a drying column and 1 to 2 bed volumes of saturated HCl/ether were passed through.

6) One to two bed volumes of saturated HCl/methanol were passed through the resin.

7) Methanol was passed through the resin until the effluent methanol has a neutral pH.

8) The resin slurry was transferred to a Soxhlet apparatus and extracted sequentially with methanol, acetonitrile, and diethyl ether, 8 hours per solvent.

The following summarizes the type of blanks obtained in this experiment.

Desorbing Solvent (elution order)	Resin Blanks 1	Resin Blanks 2	Resin Blanks 3	Reagent Blank
Ether (2 x 25 ml)	X	X	X	X
Methanol (2 x 10 ml)	X	X	X	X
Ether (2 x 10 ml)	X	X		X
Saturated HCl/ether (2 x 25 ml)	X	X		X
0.1N HCl/methanol (2 x 25 ml)	X	X		X
Saturated HCl/methanol (2 x 25 ml)	X	X	X	X

(Note: "X" indicates that the solvent was used.)

Note that resin blanks 1 and 2 correspond to duplicate blanks using a modified procedure of that employed by J. Fritz and G. Junk of Iowa State University for the concentration of anionic and neutral components from water. The modification consisted of eluting with saturated HCl/methanol in the final step, which was found necessary to elute humic substances concentrated by the resin. In this scheme, the initial eluant is ether, followed by methanol to remove any excess water, and ether to remove the methanol. Saturated HCl/ether and 0.1N HCl methanol are used in that order as subsequent eluants to elute acidic compounds from the resin. Finally, saturated HCl/ methanol is used as the eluant for the purpose cited above.

Resin 3 used an abbreviated desorption procedure consisting of ether, methanol and saturated HCl/methanol. This resin procedure was adequate to desorb neutrals in the ether and acidic compounds and humic substances in the saturated HCl/methanol. The intermediate methanol eluant served to dry the resin and was discarded. It is worth mentioning that if excess ether eluant was used, the methanol was not always necessary to dry the resin since the ether removed the water.

Reagent blank refers to the concentration of the same amounts of each solvent used in the desorption scheme, without having passed these solvents through the resin. The proposed scheme was to concentrate each of the eluants of a water bath at 60°C to less than 5 mls and blow down to 1 to 2 ml with pure nitrogen. Acidified eluants were then subjected to diazomethane esterification and again blown down to 1 to 2 ml.

Ether eluants were analyzed by GC/MS using a capillary column (Appendix F). Normal pentadecane ($n\text{-}C_{15}H_{32}$) was added to each final concentrate in the amount of 5 ug as an internal standard. For quantification purposes, the response factor of the compounds identified by GC/MS analysis relative to n-pentadecane was assumed to be equal to one.

The results of these analyses are summarized in Tables 12 through 18. Note that the estimated amounts of each compound are given in terms of micrograms per gram of dry resin. In a normal resin·separation/concentration procedure, these amounts would be the same independent of the amount of water passed through the resin. Note also that some peaks have not been identified.

Tables 12 through 14 summarize data from the resin blanks. Table 15 summarizes the data for the reagent blank. Table 16 lists those compounds found which were common to both the reagent and resin blanks. Table 17 lists those compounds found in the resin blanks but not in the reagent blank.

Table 17 is important since it lists those compounds that may be true artifacts from the resin. Noteworthy in this data is the compound found at a retention time of approximately 6.1 minutes, since the amount estimated from the average of three resin runs was 28 ug/g of dry resin. A computer search for identification of the mass spectra corresponding to this compound gave no good matches. Manual interpretation of the spectra was also attempted, but no identification was made. (Discussion with EPA in Cincinnati indicated that this compound may be a lactone.)

It was not possible to introduce the eluants containing HCl into the GC column without prior treatment, because HCl would damage the column. Therefore, diazomethane (which is used to esterify acidic organic compound) was added in excess to destroy any residual hydrochloric acid. This was attempted by adding diazomethane to esterify any acidic compounds that might be present, at the same time destroying any HCl present. Both the HCl/ether and 0.1N HCl/methanol eluants required the addition of about 10 ml of diazomethane solution for the persistence of a yellow color. The saturated HCl/methanol (normality of the concentrated HCl/methanol titrated to be 12.2N) required about 30 ml diazomethane, and the yellow color kept fading even after the addition of that amount of diazomethane. A separate portion of 30 ml of diazomethane (diazomethane blank) was also concentrated for anaysis to determine the extent of contamination due to the diazomethane itself, or the glassware. All of these eluants were concentrated to 2.0 ml and spiked with 5 ug of internal standards (n-undecane and n-pentadecane) prior to analysis by capillary GC.

GC-FID determinations of the ether eluants were also made. These included a reagent blank and three resin blanks. The blanks were all relatively clean. Two peaks (not present in the reagent blank) were identified as probable contaminants in the resin blank chromatograms. The raw data from these chromatograms are summarized in Table 18.

TABLE 12. RESIN BLANK #1 FOR DETERMINATION OF ARTIFACTS

Peak Number	Compound	Approximate Retention Time (minutes)	Amount Per Gram of Dry Resin (ug/g)
1	1,1-diethoxyethane	3.8	6.8
2	Unknown	4.1	0.2
3	Toluene	4.5	0.8
4	Unknown	5.2	0.2
5	3-methoxy-2-butanol or 1-methoxy-2-butanol or 4-methyl-2-hexanol or 2-methyl-2-pentanol	5.3	0.2
6	2-hexanol or methyl isobutyl carbinol	5.4	0.2
7	2-ethoxy-1-propanol	5.6	3.1
8	Ethyl acetate	5.7	2.8
9	Unknown	6.1	25.2
10	Ethyl benzoate	12.1	0.8

TABLE 13. RESIN BLANK #2 FOR DETERMINATION OF ARTIFACTS

Peak Number	Compound	Approximate Retention Time (minutes)	Amount Per Gram of Dry Resin (μg/g)
1	1,1-diethoxyethane	3.9	21.8
2-1	Toluene	4.6	0.9
2-2	Unknown	5.2	0.2
3	3-methoxy-2-butanol or 1-methoxy-2-butanol or 4-methyl-2-hexanol or 2-methyl-2-pentanol	5.4	0.4
4	2-hexanol or methyl isobutyl carbinol	5.5	0.6
5	2-ethoxy-1-propanol	5.6	4.2
6	Ethyl acetate	5.7	2.1
7-1	Unknown	6.1	21.3
7-2	2-methyl-2-pentanol or 2,3-dimethyl-2-butanol	7.1	0.3
8	Ethyl benzoate	12.1	0.7
9	Dibutylphthalate	19.3	1.5

TABLE 14. RESIN BLANK #3 FOR DETERMINATION OF ARTIFACTS

Peak Number	Compound	Approximate Retention Time (minutes)	Amount Per Gram of Dry Resin (ug/g)
1	1,1-diethoxyethane	3.8	5.7
2	Unknown	4.1	0.3
3	Toluene	4.5	1.0
4	Unknown	5.2	0.4
5	3-methoxy-2-butanol or 1-methoxy-2-butanol or 4-methyl-2-hexanol or 2-methyl-2-pentanol	5.4	0.4
6	2-hexanol or methyl isobutyl carbinol	5.5	0.6
7	2-ethoxy-1-propanol	5.6	3.0
8	Unknown	6.1	36.0
9	Ethyl benzoate	12.0	1.0
10	Dibutylphthalate	19.2	1.3

TABLE 15. REAGENT BLANK (ETHER) FOR DETERMINATION OF IMPURITIES

Peak Number	Compound	Approximate Retention Time (minutes)	Amount Per Gram of Dry Resin (ug/g)
1	1,1-diethoxyethane	3.9	20.9
2	NI*	4.1	0.5
3	Acetaldehyde diethylacetal or 2-ethoxy-1-propanol or 1-propoxy-2-propanol or 2-(2-ethoxyethoxy)ethanol	4.3	0.2
4	Toluene	4.5	1.8
5	1-isopropoxy-2-propanol	4.6	0.4
6	2-methyl-2-pentanol or 1,2-butanediol	4.7	0.5
7	3-methoxy-2-butanol or 1-methoxy-2-butanol or 4-methyl-2-hexanol or 2-methyl-2-pentanol	5.4	0.7
8	2-hexanol or methyl isobutyl carbinol	5.4	0.9
9	2-ethoxy-1-propanol or 1-isopropoxy-2-propanol	5.6	13.7
10	Ethyl acetate	5.7	20.3
11	2-methyl-2-pentanol or 2,3-dimethyl-2-butanol	7.2	0.4
12	Dibutylphthalate or isomer	19.6	0.9

*NI = Not Identified

TABLE 16. COMPOUNDS COMMON TO THE REAGENT (ETHER) BLANK AND THE RESIN BLANKS

Compound	Approximate Retention Time (minutes)	Amount Per Gram of Dry Resin: Resin Blank Average (μg/g)	Amount Per Gram of Dry Resin: Reagent Blank* (μg/g)
1,1-diethoxyethane	3.9	3.8	20.9
Toluene	4.5	0.9	1.8
3-methoxy-2-butanol or 1-methoxy-2-butanol or 4-methyl-3-hexanol or 2-methyl-2-pentanol	5.3-5.4	0.3	0.7
2-hexanol or methyl isobutyl carbinol	5.4	0.5	0.9
2-ethoxy-1-propanol**	5.6	3.4	13.7
Ethyl acetate	5.7	1.6	20.3
2-methyl-2-pentanol or 2,3-dimethyl-2-butanol	7.1	0.1	0.4

Notes:

* The amount per gram of dry resin for the reagent blank is a hypothetical amount based on an assumed amount of dry resin equal to that used in the resin blanks and is used only to provide a basis for comparison.

** Identification in reagent blank not as certain as in resin blanks.

TABLE 16. COMPOUNDS COMMON TO THE REAGENT (ETHER) BLANK AND THE RESIN BLANKS

Compound	Approximate Retention Time (minutes)	Amount Per Gram of Dry Resin: Resin Blank Average (μg/g)	Amount Per Gram of Dry Resin: Reagent Blank* (μg/g)
1,1-diethoxyethane	3.9	3.8	20.9
Toluene	4.5	0.9	1.8
3-methoxy-2-butanol or 1-methoxy-2-butanol or 4-methyl-3-hexanol or 2-methyl-2-pentanol	5.3-5.4	0.3	0.7
2-hexanol or methyl isobutyl carbinol	5.4	0.5	0.9
2-ethoxy-1-propanol**	5.6	3.4	13.7
Ethyl acetate	5.7	1.6	20.3
2-methyl-2-pentanol or 2,3-dimethyl-2-butanol	7.1	0.1	0.4

Notes:

* The amount per gram of dry resin for the reagent blank is a hypothetical amount based on an assumed amount of dry resin equal to that used in the resin blanks and is used only to provide a basis for comparison.

** Identification in reagent blank not as certain as in resin blanks.

TABLE 17. COMPOUNDS FOUND IN RESIN BLANKS BUT NOT IN THE REAGENT BLANK

Compound	Approximate Retention Time (minutes)	Average Amount Per Gram of Dry Resin (g/g)
NI*	4.1	0.2
NI	5.2	0.3
NI	6.1	28
Ethyl benzoate	12.0	0.8
Dibutylphthalate	19.3	0.9

*NI = Not Identified

TABLE 18. GC-FID DETERMINATIONS

Retention Time (minutes)	Area	Area Percent
Reagent Blank:		
3.04	1480	61.157 - Solvent impurity
5.05	320	13.223 - Solvent impurity
9.54	295	12.190 - Internal standard, C_{11}
15.46	325	13.430 - Internal standard, C_{15}
Resin Blank #1:		
3.04	1864	3.409 - Solvent
3.50	47680	87.197 - Resin artifact
9.52	2102	3.844 - Internal standard, C_{11}
10.74	1165	2.131 - Resin artifact
15.45	1880	3.420 - Internal standard, C_{15}
Resin Blank #2:		
3.12	3010	6.229 - Solvent
3.58	40570	83.956 - Resin artifact
9.52	2083	4.311 - Internal standard, C_{11}
10.75	892	1.846 - Resin artifact
15.46	1768	3.659 - Internal standard, C_{15}
Resin Blank #3:		
3.12	2060	3.122 - Solvent
3.58	59430	90.063 - Resin artifact
9.53	1959	2.969 - Internal standard, C_{11}
10.75	827	1.253 - Resin artifact
15.45	1711	2.593 - Internal standard, C_{15}

The peak at 10.74 and 10.75 minutes probably was ethyl benzoate, which was also found in the GC/MS analyses of ether blanks. The larger peak at 3.50 to 3.58 minutes may correspond to the major unidentified compound in the GC/MS analyses. The estimated amounts of these artifacts were as follows:

Peak R.T.	Average Amount Per Gram of Dry Resin
3.50-3.58 min.	20.1 µg
10.75 min.	0.39 µg

These amounts compare well with the amounts of these compounds found in the GC/MS determinations.

In general, both the GC/MS and GC-FID analyses showed that impurities from the resin blanks were comparable to those in the reagent blank. For the GC/MS runs, several impurities were even present at a higher concentration in the reagent blank than in the resin blanks. It is noteworthy that the amount of ethyl acetate found in the blanks was much less than that found in the previous blank experiment, which can be attributed to the use of freshly distilled ether to reduce the presence of peroxides and, possibly, acetic acid.

Previous resin studies indicated that artifacts originating from the resin may be present in the HCl/ether and HCl/methanol eluants. The concentrated eluants consistently showed a yellowish color. While its intensity diminished with use and repeated resin cleanups, the yellowish color was a persistent phenomenon throughout the studies. In addition, as a consequence of efforts to analyze 2,4-dichlorophenol, it was found that benzoic acid was present at high concentrations in a 0.1N HCl/methanol resin blank, but only traces were found in a 0.1N HCl/methanol reagent blank. Based on these findings, it was decided to perform an experiment for the specific purpose of evaluating the effectiveness of various cleanup procedures in producing low level contamination in the acidic eluants.

A batch of 20 to 40 mesh XAD-4 anionic resin that had never been used was selected for this experiment. The resin was used both "as is" (i.e. no in-house cleanup; used as received from the Ames Laboratory) and after cleanup by two different procedures as follows:

1) Gravity flow cleanup in a separatory funnel using saturated HCl in both ether and methanol

2) 8-hour Soxhlet extraction with methanol

3) 8-hour Soxhlet extraction with acetonitrile

4) 8-hour Soxhlet extraction with diethyl ether

5) Separation of cleaned resin at this point into two equal portions, as follows:

    a) One portion further cleaned by Soxhlet extraction for 24 hours with methylene chloride

    b) Second portion given no further cleanup

Duplicate columns were then prepared using the following types of resin.

1) Resin as received from Ames Laboratory (no further cleanup)

2) Resin cleaned with all solvents except methylene chloride

3) Resin cleaned with all solvents including methylene chloride

The duplicate columns were prepared with each type of resin for the purpose of performing the experiment after passage of salted and unsalted water through the resin.

Prior to loading the resin into each column, the last traces of solvent were removed by washing with methanol and water. Ten cm^3 of resin were used in each column as for previous experiments, and each was converted to the hydroxide form by passing 75 ml of 0.1N NaOH through the column, followed by 100 ml deionized (Millipore Super Q) water until the pH of the rinse water was neutral. Then, one liter of deionized water with and without salts was passed through each pair of duplicate columns at 48 B.V./hr.

Desorption of each column was as follows:

1) 2 x 25 ml ether

2) 2 x 25 ml methanol

3) 2 x 25 ml ether

4) 2 x 25 ml 0.1N HCl/ether

5) 2 x 25 ml 0.1N HCl/methanol

6) 2 x 25 ml saturated HCl/methanol

The acidic solvents were concentrated by K-D evaporation and the residues both weighed and visually observed. The results of the weighings for this experiment were as summarized in Table 19.

As can be seen from Table 19, the resins, which had been exposed to salted water, generally gave residues several times higher than for resins not exposed to salted water. The residues for the resins not exposed to salted water were generally comparable to those found for the corresponding reagent (solvent) blanks.

Of more significance were the general appearances of the concentrated eluants. While detailed observations were made on each eluant, it is sufficient to state here that the 0.1 N HCl/MeOH resin eluants all gave colored residues (yellow-brown for "unsalted" resins and dark brown for "salted" resins). The reagent blank gave only a very slight yellowish residue. It was thus concluded that the initial cleanup using a single HCl/methanol wash was probably insufficient, and that the added methylene chloride cleanup, while of possible importance, was not the only change needed in the cleanup procedure. Later laboratory studies indicated that repeated washings with saturated HCl/methanol would be necessary to obtain complete cleanup and to avoid the presence of artifacts in acidic eluants.

In order to better understand the magnitude of this yellow-brown residue, a spectrophotometric method was used to measure the absorbance of each cleanup step. Fifteen grams of dry 20 to 40 mesh XAD-4

TABLE 19. RESULTS OF WEIGHING ONE-PIECE CONCENTRATORS BEFORE AND AFTER CONCENTRATIONS

	#1 (A)	#2 (B)	#3 (C)	#4 (D)	#5 (#)	#6 (F)	Blank
	no clean-up		clean up w/o CH_2CL_2		clean-up w/ CH_2CL_2		solvent concentrated down
Solvent	--	salts	--	salts	--	salts	
0.1 N HCl/ether							
After	142.4981	141.5364	141.1961	140.3359	141.9855	145.3014	no blank done
Before	142.4969	141.5314	141.1945	140.3298	141.9840	145.1946	
Difference	0.0012	0.0050	0.0016	0.0061	0.0015	0.0068	
0.1 N HCl/MEOH							
After	142.4885	141.6068	141.1967	140.3866	142.0101	145.3714	146.4783
Before	142.4850	141.5388	141.1959	140.3270	142.0047	145.3045	146.4762
Difference	0.0035	0.0680	0.0008	0.0596	0.0054	0.0669	0.0021
Sat.d HCl/MEOH							
After	78.9745	78.4054	78.0362	77.1822	78.8190	82.1537	83.3042
Before	78.9702	78.3804	78.0186	77.1647	78.8109	82.1338	83.2957
Difference	0.0043	0.0250	0.0176	0.0175	0.0081	0.0199	0.0085

Quaternary resin was cleaned up 11 times with 20 ml each of saturated HCl/methanol. A 5 cm cell length was used at a 332 nm wavelength to measure the absorbance.

Sample	Absorbance
Saturated HCl/methanol blank	0.184
Wash 1	1.251
Wash 2	0.963
Wash 3	0.738
Wash 4	0.639
Wash 5	0.519
Wash 6	0.456
Wash 7	0.438
Wash 8	0.390
Wash 9	0.368
Wash 10	0.315
Wash 11	0.348

It appeared that after Wash 9, a plateau was reached (approximately twice the absorbance as the blank) but the conclusion can be drawn that this type of resin contamination can be cleaned up with successive acidic solvents.

7.4 RECOVERY OF LEAD

This study was conducted by adding lead nitrate to water. The pH was adjusted to 2.5 to avoid chemical precipitation of lead as the hydroxide. Salts were not added in this experiment, since it was decided that the presence of sulfate in the salts might cause the lead to precipitate as lead sulfate.

The experiment consisted of triplicate runs involving the passage of 1 liter of water containing 25 ppb of lead through the 10 cm^3 of resin at a flow rate of 48 B.V./hr. Analyses of the effluent waters were performed by atomic absorption (furnace). Results of this experiment are summarized in Table 20 and Section 6.9.

From these results, it can be seen that the average amount of lead present in the effluents from the three resins was only slightly less than that present in the influent water. The 95% confidence interval on these results include 25, so that at this level, there is no basis to conclude that any of the lead was removed by the resin.

In accordance with conversations with the EPA, it was necessary to repeat the lead study at pH 6 to 7, in order to evaluate the resin under conditions similar to those used for resin adsorption (pH=7). Previous experiments were conducted at pH 2.5 in order to reduce the likelihood of pH being a signficant variable.

Conditions of this experiment were similar to those reported in previous lead studies. Three replicates and a blank were included in

TABLE 20. RESULTS OF LEAD RECOVERY STUDY

	Concentration of Lead in Effluent Water (µg/l)	Average (µg/l)	95 Percent C.I. (µg/l)
Resin A	22.5	23.2	23.2 ± 2.53
Resin B	24.4		
Resin C	22.8		
Method Blank 1	0.18		
Method Blank 2	0.43		
Resin Blank	1.03		
15 µg/l check standard	15.4		
20 µg/l check standard	20.7		
30 µg/l check standard	30.6		

C.I. = Confidence Interval

the present study. Humic substances were not added, so as to better focus on the effect of pH. Salts were also not added, due to the possibility of lead precipitating as lead sulfate.

The results of the analyses of the effluents were as follows:

Replicate Number	Concentration of Lead in Effluent (ug/l)
1	<1
2	<1
3	<1
Resin Blank	<1

Check standards at a nominal concentration of 25 ug/l were also analyzed and gave the following results.

Check Standard	Lead (ug/l)
1	33
2	31
3	33
4	32

While the results for check standards were somewhat high, the extremely low results for the three replicates of lead in the effluent waters from the resins clearly indicate that lead is being removed from the water upon passage through the resin.

In order to determine whether the mechanism for removal might be due to the precipitation of lead as lead hydroxide and subsequent removal by the resin acting as a filter, samples of water with a pH of 6 to 7 and a lead concentration of 25 ug/l were prepared and filtered through a 0.45 um Metricel membrane filter. The results of this experiment were as follows:

	Lead Concentration (ug/l)
Before Passage	26.1
After Passage	5.01

These results indicate that lead is removed by the membrane filter, and the pH value of 6 to 7 may be causing lead to precipitate as the hydroxide.

It is uncertain just how relevant the results for these resin studies are to actual drinking waters, since lead in drinking water would likely be in solution and would have had time to reach equilibrium. Tests on actual drinking waters with background levels of lead would provide more definite answers to these questions.

Subsequent conversations with the EPA indicated the need to determine if the presence of humic substances had any effect on the behavior of lead, since it is known that humic substances can act as chelating agents for heavy metals. An experiment was, therefore, planned to evaluate the recovery of lead in the presence of humic substances.

The experimental design consisted of setting up duplicate resin columns for the concentration of 1 liter of aqueous solution containing 25 ug/l of lead as lead nitrate. Two other resin columns were used to test the 25 ug/l lead plus 2,000 ug/l of humic substances. One resin blank, which contained no lead or humic substances, was performed. The pH of these solutions was adjusted to 6 to 7. No salts were added due to the possibility of precipitating lead as one of the salts, particularly as lead sulfate which is known to have a very low solubility in water. One major change in these experiments was that each column was rinsed with 2 x 25 ml solution of 0.1N HCl. The purpose of this rinse solution (prior to the ether rinse) was to remove any lead that may have been physically removed by the resin.

The results of the analyses of the effluent waters and 0.1N HCl rinses are tabulated below:

	Concentration of Lead in Effluent Water (ppb)	Concentration of Lead in 0.1N HCl Rinse (ppb)
Resin A (without humics)	less than 1.0	22.3
Resin B (without humics)	less than 1.0	20.4
Resin C (2,000 ppb humics)	3.8	17.9
Resin D (2,000 ppb humics)	4.0	18.4
Resin blank	less than 1.0	5.4
Reagent blank	1.1	2.0

This data indicates recoveries of 82 to 90%, but as can be seen, lead is removed from water due to the initial precipitation of this element. This phenomenon might not occur in real field sampling since all lead compound should be in dissolved forms.

7.5 CONCENTRATION OF MODEL COMPOUNDS IN ABSENCE OF HUMIC SUBSTANCES AT 120 TO 150 BED VOLUMES/HOUR

Resin studies using XAD-4 Quaternary resin in the hydroxide form wre performed several times at 150 B.V./hr at various concentrations of the model compounds. The primary objective of these studies was to make a preliminary evaluation of the separation and concentration capacity of the XAD-4 Quaternary (OH-) resin for the model compounds. Emphasis was thus placed on the measurement of each compound in the final eluant concentrate. However, whenever convenient, analyses were also made of the aqueous effluent and reservoir to provide for more complete mass balances.

The results of the first study (Appendix I) are presented in Table 21. Corrections for extraction efficiency have been made for

TABLE 21. RESIN EXPERIMENTS WITH XAD-4 QUATERNARY (OH^-)
(Flow: 150 BV/Hour)

Model Compounds and Spike Concentrations		Percent Recovered From Resin Eluant	Percent Recovered From Aqueous Effluent	Percent Recovered From Reservoir	Total Percent Mass Balance
Isophorone	A	80.6	0.1	0.1	80.8
500 ug/l	B	73.8	0.1	0.1	74.0
	C	77.2	0.1	0.1	77.4
Biphenyl	A	75.0	0.1	0.1	75.2
596 ug/l	B	68.9	0.1	0.1	69.1
	C	71.3	0.1	0.1	71.5
1-Chlorododecane	A	41.4	14.1	0.1	55.6
502 ug/l	B	42.2	23.5	0.1	65.8
	C	44.4	14.0	0.1	58.5
2,6-di-tert-Butyl-4-methylphenol	A	65.5	2.0	0.1	67.6
696 ug/l	B	59.6	2.0	0.1	61.7
	C	61.5	0.05	0.4	61.9
2,4'-Dichlorobiphenyl	A	69.8	2.4	0.1	72.3
404 ug/l	B	63.6	2.4	0.1	66.1
	C	66.8	1.1	0.3	68.2
2,2',5,5'-Tetrachlorobiphenyl	A	55.0	17.3	0.2	72.5
172 ug/l	B	48.0	18.9	0.1	67.0
	C	52.7	10.9	0.2	63.8
bis(2-Ethylhexyl)phthalate	A	57.3	25.1	1.2	83.6*
668 ug/l	B	52.8	25.6	1.3	79.7
	C	55.5	13.9	contaminated	69.4
Anthraquinone	A	109	not analyzed	not analyzed	109
50.0 ug/l	B	93.4	not analyzed	not analyzed	93.4
	C	101	not analyzed	not analyzed	101
Furfural	A	51.0	21.2	not analyzed	72.2
52.44 ug/l	B	59.2	15.7	not analyzed	74.9
	C	58.9	19.7	not analyzed	78.6

(Continued)

TABLE 21. (Continued)

Model Compounds and Spike Concentrations		Percent Recovered From Resin Eluant	Percent Recovered From Aqueous Effluent	Percent Recovered From Reservoir	Total Percent Mass Balance
Chloroform	A	97.1	36.5	not analyzed	134
48.74 ug/l	B	57.2	4.0	not analyzed	61.2
	C	55.5	4.0	not analyzed	59.5
Methyl isobutyl ketone	A	81.6	not analyzed	not analyzed	81.6
50 mg/l	B	82.1	not analyzed	not analyzed	82.1
Quinoline	A	88.0	not analyzed	not analyzed	88.0
48.84 mg/l	B	85.5	not analyzed	not analyzed	85.5
Caffeine	A	14.5	39.5	not analyzed	54.0
52.30 mg/l	B	15.0	35.3	not analyzed	50.3
	C	42.4*	34.6	not analyzed	77.0
Glycine	A	not analyzed	67.5, 35.0	not analyzed	67.5, 35.0
19.74 mg/l, 9.7 mg/l	B	not analyzed	88.6, 87.6	not analyzed	88.6, 87.6
	C	not analyzed	107, 109	not analyzed	107, 109
Glucose	A	not analyzed	98.4	not analyzed	98.4
9.8 mg/l	B	not analyzed	79.4	not analyzed	79.4
Quinaldic Acid	A	16.3	not analyzed	not analyzed	16.3
49.1 ug/l	B	11.0	not analyzed	not analyzed	11.0
	C	23.6	not analyzed	not analyzed	23.6
Trimesic Acid	A	94.4	not analyzed	not analyzed	94.4
53.9 ug/l	B	64.6	not analyzed	not analyzed	64.6
	C	100	not analyzed	not analyzed	100
Stearic Acid	A	30.3	not analyzed	not analyzed	30.3
54.0 ug/l	B	20.7	not analyzed	not analyzed	20.7
	C	26.4	not analyzed	not analyzed	26.4

NOTES: *Eluted with methanol

Complete mass balances were not done on all experiments sinces these planned as preliminary evaluations.

analyses of aqueous effluent portions of certain model compounds included in Table 21. All data have been rounded to three significant figures.

Twenty of the 22 model compounds were evaluated during the first study. Note that methyl isobutyl ketone, quinoline and caffeine concentrations are approxiamtely 50 mg/l rather than 50 ug/l. Glycine was studied at 10 and 20 mg/l, and glucose was studied at 10 mg/l. Many of the results for the 20 compounds studied confirmed expectations but, in some cases, the results are surprising. Table 22 presents the classification of compounds which we believe best characterizes the nature of the model compounds.

Most hydrophobic neutral compounds showed strong concentration by the resin according to the adsorption mechanism (Van der Waals attraction) characteristic of non-ionic polymer resins. In other words, the anionic exchange capacity of the XAD-4 Quaternary resin did not seem to affect (either favorably or unfavorably) its capacity to absorb neutral organic compounds.

One hyrophobic neutral compound which showed low recovery in the eluant concentrate was 1-chlorododecane. Chriswell, et al. (JAWWA, 669-674, December 1977) reported an even lower recovery of dodecane on XAD-2 resin, but the reason for the low recovery of thse aliphatic hydrocarbons is not clear. One possibility is that the aliphatic hydrocarbons absorb onto particulates (i.e. from added salts or other contamination) and pass through the resin in a "micelle" form.

While recoveries of 2,2',5,5'-tetrachlorobiphenyl and bis(2-ethylhexyl)phthalate were both good, a reasonable amount of each of them was also recovered from the water. It is possible that the flow rate for aqueous samples has affected the efficiency with which the compounds are sorbed by the resin. This is also true for the compounds furfural and caffeine, although due to their hydrophilic character, one might expect to find some in the water.

A high percentage of hydrophobic base quinoline was recovered in the resin eluant, which corresponded to expectations. G. A. Junk, et al. (1) reported similar high recovery (84%) with XAD-2 resin.

Compounds classified as hydrophobic acids include stearic acid, trimesic acid, 2,4-dichlorophenol, and 5-chlorouracil. Acids, in general, have posed problems due to their tendency to form salts. The XAD-4 Quaternary resin has the capacity to adsorb acids by two mechanisms - Van der Waals adsorption and anion exchange. This is indicated by the high (86.3%) average recovery of trimesic acid in the resin eluant. Elution for acids was with HCl saturated ether. Stearic acid showed much lower average recovery (25.8%) in the resin eluant. It is interesting to note that the British Water Research Centre (9) found stearic acid recoveries of 20.8 to 25.8% at pH 2, and 4.8% at H 8.5 when using XAD-2 resin. The pH of the water in our work was 7.0, indicating that the anion exchange mechanism might have had some importance, but also that the Van der Waals adsorption mechanism might be predominant. Possibly the same reason for low recovery of the aliphatic hydrocarbon dodecane is at work here, since stearic acid has a strong aliphatic nature in addition to an acid functional group.

TABLE 22. CLASSIFICATION OF MODEL COMPOUNDS

Hydrophobic Neutrals

- 2,4'-dichlorobiphenyl
- 2,2'-5,5'-tetrachlorobiphenyl
- bis(2-ethylhexyl)phthalate
- 1-chlorododecane
- biphenyl
- isophorone
- anthraquinone
- methyl isobutyl ketone
- 2,6-di-tert-butyl-4-methylphenol
- phenanthrene

Hydrophobic Acids

- stearic acid
- trimesic acid
- 2,4-dichlorophenol
- 5-chlorouracil

Hydrophobic Base

- quinoline

Hydrophilic Neutrals

- glucose
- furfural
- chloroform

Hydrophilic Acid

- quinaldic acid

Hydrophilic Base

- caffeine
- glycine

Quinaldic acid, while partially recovered, was present in a lower average%age (17.0) than anticipated. It is hypothesized that a "zwitterion" of qunialdic acid may be forming in aqueous solution, causing the molecule to have a positive as well as negative charge, thereby, reducing the tendency toward anion exchange.

The HCl/ether concentrates of the acids were analyzed by GC/MS to confirm the identity of the derivatized acid peaks. The GC/MS results confirmed the identity of these peaks, and incorrect peak identification did not appear to be a problem.

The hydrophilic neutrals were classified as problem compounds, but these preliminary results show surprisingly good recovery for all compounds except glucose. Average recoveries of furfural and chloroform were 56.4 and 69.9%, respectively.

Finally, the hydrophilic bases (caffeine and glycine) proved to be difficult to separate and concentrate from aqueous solution using the XAD-4 Quaternary resin. There is some indication that recovery of caffeine can be improved by eluting with methanol. Glycine was not analyzed in the resin eluant since most of it was accounted for (87.7%) in the analysis of the aqueous effluent.

Second Experiment for Concentration of Seven Model Compounds in Absence of Humic Substances (120 to 150 Bed Volumes/Hour)

During the second experiment, seven neutral and acidic compounds were studied on a 1 liter bench scale. The concentrations of methyl isobutyl ketone, caffeine, and quinoline were dropped to approximately 50 ug/l and phenanthrene was added at 1.01 ug/l.

This experiment was performed under the same conditions used previously for characterizing the behavior of model compounds (Appendix I) except for a change in the resin desorption (elution) procedure. Desorption was accomplished in two stages:

1) Twenty-five milliliters of freshly distilled ether was added to the resin column and the column shaken for 5 minutes to dislodge the resin. After shaking, the resin was allowed to stand for 5 minutes, and then the ether was drained and collected. This was followed with another 25 ml aliquot, then combined with the first extract.

2) The resin was washed out of the column with small amounts of Super-Q water into a 25 ml septum vial. Excess water was decanted, 10.0 ml of 0.1N Hcl/MeOH added and the vial sealed. Vials were placed on an orbital shaker at 1,500 RPM for 30 minutes.

The ether eluant was analyzed for neutral compounds (Section 6.3), while the HCl/MeOH eluant was analyzed for the acidic compounds (Section 6.4). 2,4-dichlorophenol was analyzed in both the ether and HCl/MeOH eluants (Section 6.3). The results of this experiment are summarized in Table 23.

TABLE 23. RESULTS FOR SEVEN MODEL COMPOUNDS AT SPECIFIED CONCENTRATION (120-150 BV/Hr Flow Rate)

Model Compounds		Percent Recovered From Resin Ether Eluant	Percent Recovered From Resin MeOH/HCl Eluant	Percent Recovered From Water	Total Percent Recovered
methyl isobutyl ketone	A	107	NA	ND	107
50.45 µg/l	B	103	NA	ND	103
	C	96.8	NA	ND	96.8
Quinoline	A	104	NA	ND	104
50.88 µg/l	B	99.1	NA	ND	99.1
	C	101	NA	ND	101
Phenanthrene	A	128	NA	ND	128
1.01 µg/l	B	107	NA	ND	107
	C	101	NA	ND	101
Caffeine	A	30.5	NA	12.5*	43.0
50.74 µg/l	B	31.4	NA	16.6*	48.0
	C	32.9	NA	15.4*	48.3
2,4-dichlorophenol	A	18.6	<3	ND	18.6
50.29 µg/l	B	11.2	<3	ND	11.2
	C	16.3	<3	ND	16.3
Quinaldic Acid	A	NA	31.5	NA	31.5
50.55 µg/l	B	NA	32.8	NA	32.8
	C	NA	29.9	NA	29.9
Trimesic Acid	A	NA	35.4	NA	35.4
50.85 µg/l	B	NA	42.5	NA	42.5
	C	NA	33.0	NA	33.0

*Data corrected for extraction efficiency of 63 percent from water at pH = 8.

ND = Not Detected

NA = Not Analyzed

Trimesic acid, quinaldic acid and 2,4-dichlorophenol were analyzed by HPLC according to the conditions listed in Appendix J.

Check standards of model compounds in water, ether and HCl/MeOH were prepared and analyzed as a quality control measure to estimate the importance of analytical error in mass balance estimations. The results of these QC check standards are shown in Table 24.

With the exception of caffeine in water, the check standard results all showed that the analytical methods were sufficiently accurate to obtain good mass balance estimates. For caffeine, previous work had already shown that the extraction efficiency of caffeine from water was about 63%, and the results for the check standard confirmed this. Therefore, data for aqueous effluents from resin had to be corrected for this source of bias in analysis.

Note that, while the amount of 2,4-dichlorophenol in the HCl/MeOH resin eluants was found to be absent or very low, calibration standard analyzed in HCl/MeOH gave good, repeatable response. Although ion-pairing chromatography does not usually work well in non-aqueous solvents, in this case the check standards showed the analytical procedure to be satisfactory.

Check standards were not performed for quinaldic and trimesic acids, but three calibration standards containing these acids were prepared in 0.1N HCl/MeOH. This was done in order to reduce any bias in calibration due to using calibration procedures different from sample analysis procedures. These analyses were performed by ion-pairing HPLC, and required neutralization of the HCl with $NaHCO_3$ prior to chromatographic injection.

These calibration standards were prepared by adding 50.5 ug quinaldic acid and 50.9 ug trimesic acid to 10 ml of 0.1N HCl/MeOH. This solution was then diluted to 1:10 with pure water, the final pH adjusted to 5 to 8 by $NaHCO_3$, and 100 ul aliquots injected for HPLC. Results are shown in Table 25. These results show that the precision for these calibration standards was quite good.

MIBK, quinoline, phenanthrene, caffeine and 2,4-dichlorophenol were analyzed by capillary GC/FID using pentadecane as an internal standard. Response factors were determined at 1, 5, 10, 20 and 40 ug/ml levels. An average response factor (vs. n-pentadecane) was also calculated for each compound (see Table 26).

Summary of Results for Bench-Scale Evaluation of Model Compounds

At this stage, it is perhaps useful to summarize the results (Table 27) for evaluation of the capacity of the XAD-4 anionic resin at the bench-scale level. Not included in Table 27 are the acidic compounds (quinaldic, trimesic and stearic acids, and 2,4-dichlorophenol). Also not included in the table is 5-chlorouracil, which has been found to be unstable in water and difficult to evaluate. This

TABLE 24. ANALYTICAL QA/QC

Compound	Spike level, μg	Found levels, μg	Average Percent Recovery
Check Standards in Ether			
methyl isobutyl ketone	49.7	50.0,54.3,54.2	106
quinoline	50.1	56.8,57.1,56.7	114
phenanthrene	0.99	1.14,1.00,1.09	109
caffeine	50	60.9,54.6,57.6	115
Check Standards in Water			
2,4-dichlorophenol	50.3	54.6,47.9,49.2	101
quinoline	50.9	49.4,49.8,46.9	95.7
phenanthrene	10.1	0.950,0.879,0.805	86.9
caffeine	50.7	34.5,32.2,28.8	62.8
Check Standards in 0.1 N HCl/MeOH			
2,4-dichlorophenol	50.6	46.7,56.3,56.4	106

TABLE 25. STANDARD CALIBRATION OF QUINALDIC AND TRIMESIC ACIDS

Compound	Retention Time (min)	Area (unit)	Peak Height (mm)
Quinaldic Acid	3.37	68160	134
	3.35	66940	135
	3.40	65680	133
Trimesic Acid	6.24	5234	20.5
	6.12	5375	21
	6.05	5435	22

TABLE 26. RESPONSE FACTORS VS. n-PENTADECANE
(Conc. = 5.0 µg/ml)
Concentration (mg/ml)

	1.0	5.0	10.0	20.0	40.0	40.0	Average
MIBK	1.78	1.93	1.66	1.66	--	1.61	1.72
2,4-Dichlorophenol	4.90	3.13	2.92	2.62	2.48	2.51	2.91
Quinoline	1.33	1.20	1.17	1.16	1.15	1.14	1.19
Phenanthrene	0.876	0.854	0.824	0.84	0.785	0.782	0.826
Caffeine	3.48	3.12	2.85	2.77	2.48	2.57	2.84

TABLE 27. RESULTS OF NEUTRAL AND BASIC MODEL COMPOUNDS AT MICROGRAM PER LITER LEVELS USING XAD-4 ANIONIC RESIN

Model Compounds and Spike Concentrations		Percent Recovered From Ether Eluant	Percent Recovered From Water	Percent Recovered From Reservoir	Total Percent Recovered
Isophorone 500µg/l	A	80.6	0.1	0.1	80.8
	B	73.8	0.1	0.1	74.0
	C	77.2	0.1	0.1	77.4
Biphenyl 596 µg/l	A	75.0	0.1	0.1	75.2
	B	68.9	0.1	0.1	69.1
	C	71.3	0.1	0.1	71.5
1-chlorododecane 502 µg/l	A	41.4	14.1	0.1	55.6
	B	42.2	23.5	0.1	65.8
	C	44.4	14.0	0.1	58.5
2,6-di-tert-butyl-4-methylphenol 696 µg/l	A	65.5	2.0	0.1	67.6
	B	59.6	2.0	0.1	61.7
	C	61.5	0.05	0.4	61.9
2,4'-dichlorobiphenyl 404 µg/l	A	69.8	2.4	0.1	72.3
	B	63.6	2.4	0.1	66.1
	C	66.8	1.1	0.3	68.2
2,2',5,5'-tetrachlorobiphenyl 172 µg/l	A	55.0	17.3	0.2	72.5
	B	48.0	18.9	0.1	67.0
	C	52.7	10.9	0.2	63.8
Bis(2-ethylhexyl)phthalate 668 µg/l	A	57.3	25.1	1.2	83.6
	B	52.8	25.6	1.3	79.7
	C	55.5	13.9	contaminated	69.4
Anthraquinone 50.0 µg/l	A	109	NA[(a)]	NA	109
	B	93.4	NA	NA	93.4
	C	101	NA	NA	101

(Continued)

TABLE 27. (Continued)

Model Compounds and Spike Concentrations		Percent Recovered From Ether Eluant	Percent Recovered From Water	Percent Recovered From Reservoir	Total Percent Recovered
Furfural 52.4 μg/l	A	51.0	21.2	NA	72.2
	B	59.2	15.7	NA	74.9
	C	58.9	19.7	NA	78.6
Chloroform 48.7 μg/l	A	97.1	36.5	NA	134
	B	57.2	4.0	NA	59.2
	C	55.5	4.0	NA	57.5
Methyl isobutyl ketone 50.5 μg/l	A	107	ND(b)	NA	107
	B	103	ND	NA	103
	C	96.8	ND	NA	96.8
Phenanthrene 1.0 μg/l	A	128	ND	NA	128
	B	107	ND	NA	107
	C	101	ND	NA	101
Caffeine 50.7 μg/l	A	30.5	12.5(c)	NA	43.0
	B	31.4	16.6(c)	NA	48.0
	C	32.9	15.4(c)	NA	48.3

NOTES: (a) NA = Not analyzed
(b) ND = Not Detected
(c) Data include correction for extraction efficiency of 63 percent for caffeine from water.

table only includes those results from experiments conducted at a flow rate of 120 to 150 B.V./hr (linear velocity 25 to 32 cm/min), and adsorption/desorption scheme outlined in Appendix I.

As will be shown in the next section of this report, the acidic compounds are effectively adsorbed by the anionic exchange mechanism of the XAD-4 Quaternary resin. Evidence also indicates that desorption is achieved with either HCl/ether or HCl/methanol. Subsequent investigations in the analysis of acidic compounds, without derivatization on a free acid phase, showed that quinaldic acid is not soluble in acidic ether. Therefore, the desorption scheme in these later studies (and the pilot plant studies) would include desorption with 0.1N HCl/ether followed by 0.1N HCl/methanol.

Several experiments were designed to obtain more satisfactory results in recovery and mass balance of the acidic compounds.

A mix of the following compounds at the indicated concentrations was prepared in methanol: quinaldic acid (499 ppm), trimesic acid (499 ppm), lauric acid (100 ppm), stearic acid (50 ppm), and 2,4-dichlorophenol (501 ppm). One milliliter of this standard solution was added to a liter of pure water to give a 1,000 fold dilution.

The concentration of HCl in the HCl/ether eluant was measured to be 0.05 N, while HCl in the HCl/MeOH eluant was found to be 0.075N.

Desorption of resin was as follows:

1) 2 x 25 ml of distilled ether (would normally desorb the neutral organic compounds)

2) 2 x 10 ml of MeOH to dry resin

3) 2 x 10 ml of Et_2O/HCl to remove MeOH

4) 2 x 25 ml of Et_2O/HCl to remove acidic compounds

5) 2 x 25 ml of MeOH/HCl to remove remaining acidic compounds

This desorption scheme generally follows that used by J.J. Richard and J.S. Fritz (10) for the analysis of neutral and acidic compounds.

The aqueous solution was passed over the resin at a flow rate of 150 B.V./hr (linear velocity = 25 to 32 cm/min, residence time = 24 to 30 seconds) in order to obtain data for acidic compounds comparable to that obtained previously for the other model compounds.

The experiment was performed in triplicate, with a reagent blank and a resin blank. Check standards of compounds were also prepared in MeOH/HCl as well as Et_2O/HCl and analyzed identically to the sample eluants. This served to determine whether analytical error was significant. Results for the experiment are summarized in Table 28. Analyses were done by capillary GC-FID (Section 6.3) using internal

TABLE 28. RESULTS FOR FOUR ACIDIC MODEL COMPOUNDS
(120-150 BV/Hr Flow Rate) Humic: Not Added

Model Compounds	Percent Recovered From Ether Eluant	Percent Recovered From Ether/HCl Eluant	Percent Recovered From MeOH/HCl Eluant	Percent Recovered From Water	Total Percent Recovered
2,4-Dichlorophenol	0.42	21.0	5.56	0	27.0
500 µg	2.86	17.1	6.14	0	26.1
	0.28	12.9	20.1	0	33.3
Lauric Acid*	0	48.3	0	0	48.3
100 µg	.39	25.9	5.40	0	31.7
	0	27.7	3.73	0	31.4
Quinaldic Acid	0	3.16	89.0 (HPLC)	0.37	92.5
500 µg	0.12	2.59	99.2 (HPLC)	0.32	102
	0.09	2.44	92.4 (HPLC)	0.28	95.2
Trimesic Acid	0.31	6.70	28.6 (HPLC)	0.70	36.3
500 µg	0.33	7.15	24.2 (HPLC)	1.64	33.3
	0.45	8.58	24.2 (HPLC)	0.37	33.6
Stearic Acid	10.2	59.5	4.28	20.6	94.6
50 µg	16.0	29.2	4.58	26.4	76.2
	11.9	42.1	2.62	17.1	73.7

*Not a model compound; used as a tracer compound.

standardization in all cases except for the analysis of quinaldic and trimesic acids in MeOH/HCl eluant, which were done by HPLC (Section 6.4).

From the results in Table 28, it can be seen that the mass balance and recovery of quinaldic acid is good, while the mass balance of stearic acid is satisfactory. The recoveries of lauric acid, 2,4-dichlorophenol and trimesic acid, are all unsatisfactory.

The results for the check standards are summarized in Table 29. It is apparent from these check standards, that while analytical results for the model compounds in ether were accurate, there were several instances of inaccuracy (negative bias) in the measurement of model compounds in the HCl/ether and HCl/methanol solutions. Only quinaldic acid gave reasonable recovery in the HCl/ether solution. The measurements in HCl/methanol were somewhat better, but a large negative bias was shown for 2,4-dichlorophenol and lauric acid measurements. It was concluded that analytical error was signficant for several of the measurements on the resin eluants, and that this error makes accurate mass balance calculations impossible.

The results for quinaldic acid were considered accurate, however, since the reported measurements were made by HPLC. While there are some problems associated with HPLC, the fact that derivatization is not required may account for the improved accuracy of measurement.

Given the results on the check standards summarized in Table 29, it was decided to perform some repeat analyses of model acidic compounds in several different solvents in order to determine the precision of measurement of standard solutions. This evaluation did not include the resin. The purpose was to evaluate analytical error in the analysis of the eluants.

The experimental design consisted of the preparation of five replicate samples of each solution containing the model acid compounds. Each solution was concentrated, derivatized, and analyzed by capillary GC-FID (Section 6.3). A blank was also included for each type of solution. The experimental design is summarized in Table 30. The values in parentheses represent the micrograms of compounds (quinaldic acid, trimesic acid, and stearic acid) added to each solution.

The data in Table 30 indicates that considerably more variability was present for acid analyses than for the internal standard. Stearic acid was not recovered in the saturated HCl/ether solution, and quinaldic acid was not recovered in the 0.1N HCl/methanol.

It is apparent that precision is worse at lower concentrations when analyzing in a 0.1N HCl/methanol solution. Therefore, improved precision might be obtained by using larger amounts of the acid model compounds.

The results also indicate that care must be taken in calibration, since the variability of these results could give a large calibration bias if too few standards are used to establish the calibration factor.

TABLE 29. QUALITY CONTROL RESULTS FOR CHECK STANDARDS

Model Compounds	Spiked Amount (μg)	Amount Found	Average* Percent Recovery
Ether Standard Solutions:			
ISTD (C_{15})	10		
2,4-Dichlorophenol	500	NA	NA
lauric acid	100	101, 104	102.5
quinaldic acid	500	415, 419	83.4
trimesic acid	500	403, 398	88.2
stearic acid	50	54.2, 51.4	106
Ether/HCl Standard Solutions:			
ISTD (C_{15})	5		
2,4-Dichlorophenol	500	189, 252, 207	43.2
lauric acid	100	12.9, 13.1, 13.0	13.1
quinaldic acid	500	458, 404, 469	88.7
trimesic acid	500	288, 134, 240	44.1
stearic acid	50	24.3, 20.3, 23	45.1
MeOH/HCl Standard Solutions:			
ISTD (C_{15})	5		
2,4-Dichlorophenol	500	162, 122, 188	31.5
lauric acid	100	21.6, 14.2, 23.0	19.6
quinaldic acid	500	516, 463, 401	98.7
trimesic acid	500	518, 513, 512	103
stearic acid	50	55.7, 50.1, 54.7	107

NA = Not Analyzed
ISTD (C_{15}) = n-pentadecane

*Percent recovery of each acidic compound was calculated against known concentrations of 2,4-dichlorophenol (without concentration and derivatization) and methyl ester standard of other acidic compounds.

TABLE 30. ANALYTICAL QUALITY CONTROL FOR ACIDIC COMPOUNDS

	Number of Replicates					
	1	2	3	4	5	Blank
Saturated HCl/ether (50 μg)	xx	xx	xx	xx	xx	xx
Saturated HCl/ether, doped with Methanol (50 μg)	xx	xx	xx	xx	xx	xx
0.1 N HCl/Methanol (50 μg)	xx	xx	xx	xx	xx	xx
Saturated HCl/Methanol (50 μg)	xx	xx	xx	xx	xx	xx
0.1 N HCl/Methanol (25 μg)	xx	xx	xx	xx	xx	--

"X" represents one injection into GC

Raw data (i.e. area responses by GC) for these analyses are summarized below.

Saturated HCl/Ether

	r.t.	IA	IB	2A	2B	3A	3B	4A	4B	5A	5B	Average
QA	21.34	2886	3399	3568	3269	4080	4385	3543	3419	3390	3437	3538
TA	23.81	2017	2180	2416	2236	3260	3423	1759	1692	2299	2308	2359
SA	25.86	--	--	--	--	--	--	--	--	--	--	--
ISTD	18.76	7228	7468	7404	7058	6938	7182	7394	7110	7596	7596	7297

Saturated HCl/Ether doped with MeOH*

QA	2600	2742	3105	2954	4625	4774	3451	3640	4819	4443	3715
TA	3392	3483	3218	3055	5013	5042	4438	4466	4451	4299	4086
SA	4891	4982	5075	4804	7034	7026	5835	5785	6636	6371	5844
ISTD	7408	7436	7390	7330	7240	7220	7282	7478	7534	7248	7357

(Continued)

TABLE 30. (Continued)

	r.t.	IA	IB	2A	2B	3A	3B	4A	4B	5A	5B	Average
						0.1 N HCl/MeOH (50 µg spike)						
QA		2290	2343	--	--	1680	1763	2431	2431	2517	2594	1805
TA		7470	7630	5843	5748	7138	7234	8782	8674	7560	7698	7378
SA		9244	9374	7488	7298	8422	8604	10450	10310	8694	8862	8875
ISTD		7734	7770	7826	7984	8120	8312	9326	9328	8490	8554	8344
						0.1 N HCl/MeOH (25 µg spike)						
QA		--	--	--	--	--	--	--	--	--	--	--
TA		5262	5279	2992	2844	2007	2145	1573	1627	1961	1973	2766
SA		6016	5986	3672	3469	2530	2699	1183	1212	1649	1675	3009
ISTD		8508	8532	7462	7378	7144	7498	7324	7432	7072	6816	7517
						Saturated HCl/MeOH						
QA		7514	7248	3671	4607	7326	6822	6518	6025	2650	2772	5515
TA		6872	6624	2206	2626	6460	6078	7678	7572	3493	3493	5310
SA		2825	2728	2886	3475	3138	2958	3471	3136	3322	3378	3132
ISTD		6910	6658	6373	7070	7052	6662	6804	7122	7380	7430	6936

It is apparent from these data that while the variability of repeat injections is small, the variability among samples is significant in some cases. Taking the average values of the duplicate injections, the variability of the 5 average samples results have been calculated as the standard deviations and are summarized below as the mean, standard deviation, and percent relative standard deviation for each compound and solution.

(Continued)

TABLE 30. (Continued)

		Mean Area	Standard Deviation	Percent Relative Standard Deviation
		Saturated HCl/Ether		
QA	--	3538	410	11.6
TA	--	2359	600	25.4
ISTD TA	--	7297	197	2.69
		Saturated HCl/Ether - Doped With Methanol*		
QA	--	3715	922	24.8
TA	--	4086	779	19.1
SA	--	5844	933	16.0
ISTD	--	7357	74.2	1.01
		0.1 N HCl/Methanol (50 μg)		
QA	--	1805	1059	58.6
TA	--	7378	1056	14.3
SA	--	8875	1094	12.3
ISTD	--	8344	624	7.48
		0.1 N HCl/Methanol (25 μg)		
TA	--	2766	1481	53.5
SA	-	3009	1905	63.3
ISTD	--	7517	592	7.87

(Continued)

TABLE 30. (Continued)

		Mean Area	Standard Deviation	Percent Relative Standard Deviation
			Saturated HCl/Methanol	
QA	--	5515	2015	36.5
TA	--	5310	2237	42.1
SA	--	3132	231	7.36
ISTD	--	6936	283	4.08

QA = Quinaldic Acid
TA = Trimesic Acid
SA = Stearic Acid
ISTD = Internal standard, n-pentadecane

*10 percent methanol was added to saturated HCl/ether for possible higher derivatization conversion.

Finally, it appears that the saturated HCl/ether-doped with methanol, and the 0.1N HCl/methanol solutions gave the best overall precision and recovery for the model compounds studied.

A summary of some previous work with the acidic compounds was prepared for internal review purposes, and it was decided to include it as the next section of this report in order to provide more detail and to indicate the extent of work that has been done on these compounds.

Previous experiments had not satisfactorily characterized the behavior of 5-chlorouracil and 2,4-dichlorophenol on XAD-4 anionic resin at the specified concentration levels (i.e. 50 ug/l). After some preliminary tests to validate the proposed analytical method (HPLC) for 5-chlorouracil, an experiment was conducted under the same conditions used to evaluate the other model compounds (Appendix I), the only difference being that no HCl/ether eluant was used, only 0.1N HCl/methanol.

While results for 5-chlorouracil were somewhat inconclusive, certain facts can be clearly stated. 5-chlorouracil was not found in the effluent water, the reservoir wash, or the ether eluant.

Analysis of the 0.1N HCl/methanol eluants proved difficult. While analyses of the calibration standards gave a single peak at 3.56 minutes, the sample gave an additional interfering peak at about 2.90 minutes. The rentention time of the 5-chlorouracil became 3.91 minutes and increased during the course of the day to about 4.15 minutes. The 0.1N HCl/methanol eluants were neutralized with NaOH prior to analysis, and this neutralization step apparently introduced an impurity and caused a change in the structure of 5-chlorouracil. Thus, the experiment showed that 5-chlorouracil apparently behaves as an acid and elutes with the 0.1N HCl/methanol, with about 50% recovery indicated. However, the quantitative results were not sufficiently precise to warrant reporting specific values.

The results for the analyses of 2,4-dichlorophenol are shown in Table 31.

The mass balance results for 2,4-dichlorophenol was not good. While it is not entirely clear why the mass balance does not account for more of the dichlorophenol, it is thought that the problem is analytical, and that the procedure is effective in concentrating more of the 2,4-dichlorophenol than is indicated in the results.

Since prior work with 5-chlorouracil indicated that it might be somewhat unstable in aqueous solutions, it was decided to perform tests for the single purpose of evaluating its stability. Duplicate samples were prepared using filtered (0.45 um) Millipore Super-Q water to which 500 ppb each of 5-chlorouracil and naphthalene had been added. Naphthalene was used as an internal standard. Every 70 minutes during a 48-hour period, duplicate injections of these standard solutions were made for analysis by HPLC. Results for the experiment indicated that 5-chlorouracil remained stable during the

TABLE 31. MASS BALANCE DETERMINATION OF 5-CHLOROURACIL

Replicate	Percent Recovered From 0.1N HCl/Methanol Eluant	Percent Recovered From Ether Eluant	Percent Recovered From Water	Percent Recovered From Reservoir Rinse	Percent Recovered
A	31.4	0	0	0	31.4
B	40.2	0	0	0	40.2
C	37.8	0	0	0	37.8

period covered by the study, based on constant peak areas of 5-chlorouracil, both on an absolute basis and relative to naphthalene. Some peak splitting was observed around the 24-hour period, but this corrected itself after a while.

Results for the laboratory scale isolation/concentration of acidic model compounds on XAD-4 anionic resin at the low concentration levels specified in the project have not been sufficiently precise and repeatable. It was, therefore, decided to perform an experiment at a higher concentration level, in order to reduce the influence of analytical error on the results. It was also hoped that some of the analytical techniques used in this study would also be applicable in the pilot plant study, which used the lower concentrations specified by EPA, but which also used a total mass 500 times that of the laboratory scale experiments.

Six columns (each containing 10 cm^3 of wet resin) were prepared for use in the study. Two were used for resin blanks (one on salted water, and one on unsalted water), two were used for adsorbing the model acids dissolved in a liter of deionized water, and two were used for adsorbing the model acids dissolved in a liter of salted water. The concentrations of the quinaldic acid, trimesic acid, 5-chlorouracil and 2,4-dichlorophenol were each prepared at 5 ppm, with stearic acid prepared at 50 ppb due to concern that the solubility limit in water might be exceeded at higher concentrations. The adsorption flow rate was maintained at 48 B.V./hr. Desorption was accomplished with the following solvents.

1) 2 x 25 ml ether

2) 2 x 25 ml methanol

3) 2 x 25 0.1N HCl/methanol

4) 2 x 25 0.1N HCl/ether

The order of elution with the acidic solvents was switched from what was used previously, since tests showed that quinaldic acid is very soluble in 0.1N HCl/methanol but that a precipitate forms in the presence of 0.1N HCl/ether. This phenomena was not observed previously, since standards were always prepared in solvents other than ether.

After passage through the resin, the eluants were brought up to exactly 50 ml. A 1 ml aliquot was withdrawn for GC-FID (20 ug of n-pentadecane was added as an internal standard for calibration purposes). A 4 ml aliquot was withdrawn for HPLC analysis (Section 6.4). The remaining 45 ml of each acidic solvent was saved under refrigeration for possible use if additional analyses proved necessary.

Effluent water samples were measured volumetrically and a 10 ml aliquot was withdrawn from each sample for HPLC analysis of quinaldic and trimesic acids as well as 5-chlorouracil. The remainder was extracted by methylene chloride for analysis of stearic acid and 2,4-dichlorophenol by GC-FID (Section 6.3).

Results obtained in this experiment are summarized in Table 32.

In the analysis of the acidic methanol samples for quinaldic acid, three peaks were found in the chromatogram where only one was expected. By spiking the samples with a known amount of pure quinaldic acid, it was determined that only the middle peak area was enhanced. The integration of this peak area, however, may not be perfect because of the peaks that elute so close to it. This may account in part for the greater than 100% recovery found. Finally, the resin blanks were determined and peaks corresponding to the approximate quinaldic acid retention time found in both of them. The amount, however, was very small, corresponding to 2.40% and 1.40% of the amount added to samples. Blank correction was not made in these experiments.

In conclusion, data indicate that quinaldic acid is completely recovered in the 0.1 N HCl/methanol eluant. Recoveries of trimesic acid and 2,4-dichlorophenol were lower, and 100% mass balances were not obtained. Finally, 5-chlorouracil recoveries in the 0.1 N HCl/methanol eluants were excellent. In general, salts did not affect recovery, although 5-chlorouracil recovery was slightly higher for salted water.

In general, quinaldic acid, trimesic acid, 2,4-dichlorophenol, and 5-chlorouracil can be more accurately determined at higher concentration levels than at the EPA-specified lower concentration levels. It was thought, however, that the analytical techniques used in this experiment would be applicable (with slight modifications) when the pilot plant studies were conducted. The larger total mass in the pilot plant would permit data to be obtained at EPA-specified concentration levels.

Satisfactory data were not obtained for stearic acid. In part, this was due to the difficulty in analyzing stearic acid at low levels (i.e. 50 ug/l or less) and to the transformation of stearic acid to esters during the isolation/concentration scheme. GC/MS analyses of stearic acid standards prepared in 0.1 N HCl/methanol verified that stearic acid was converted to its methyl ester. The extent of this conversion was not clear.

Summary of Experiments on Acidic Model Compounds

The first resin experiment on acidic model compounds was performed at a flow rate of 120-150 B.V./hour. The acidic model compounds were added to water at approximately the 50 ug/l level by spiking with 1 ml of a concentrated methanol standard solution.*

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*The acidic model compounds included here were quialdic acid, trimesic acid, stearic acid, 2,4-dichlorophenol, and 2,6-di-tert-butyl-4-methyl phenol. This latter compound was subsequently dropped from the acidic compound list, since it was judged to have a predominantly neutral character.

TABLE 32. BENCH-SCALE EVALUATIONS OF MODEL COMPOUNDS
(48 BV/Hr Flow Rate

Model Compounds Spiked at 5 mg/l		Percent Recovered in 0.1 N HCl/Methanol Eluant	Percent Recovered in 0.1 N HCl/Ether Eluant	Percent Recovered In Water	Percent Recovered In Reservoir	Total Percent Recovered
Quinaldic Acid in	A	118	2.7	ND	NA	121
unsalted water	C	121	ND	ND	NA	121
Quinaldic Acid	B	122	ND	ND	NA	122
in salted water	D	113	ND	ND	NA	113
Trimesic Acid	A	46.3	ND	ND	NA	46.3
in Unsalted Water	C	47.2	4.6	ND	NA	51.8
Trimesic Acid	B	50.6	3.0	ND	NA	53.6
in Salted Water	D	46.8	5.5	ND	NA	52.3
2,4-dichlorophenol	A	59.6	6.94	ND	ND	66.6
in unsalted water	C	66.0	5.62	ND	ND	72.4
2.4 dichlorophenol	B	60.0	6.46	ND	ND	66.4
in salted water	D	60.2	5.62	ND	ND	65.8
5-chlorouracil in	A	83.3	NA	NA	NA	83.3
unsalted water	C	74.7	NA	NA	NA	74.7
5-chlorouracil in	B	90.1	NA	NA	NA	90.1
salted water	D	92.3	NA	NA	NA	92.3

Note: Ether and methanol eluants were not analyzed.

Concentration by K-D evaporation of the saturated HCl/Ether eluant gave a yellow, oily, sweet-smelling residue in all three samples and a brown floc in the resin blank. Concentration of a portion of HCl/Ether gave a slight white residue but none of the yellow oily material, indicating that the resin contributed to the presence of the contamination. Further tests indicated that the oily residue persists even when a resin is used a second time for concentration.

It was thought that the presence of acetate impurities in the water might have contributed to the contamination, but tests with acetate-free water also resulted in the formation of a yellow or brown viscous, sweet-smelling liquid. Due to the contamination, it was not possible to analyze for these compounds, and the experiment was terminated.

Tests were made to determine the extraction efficiency of the carboxylic acids from water. 3 x 100 ml portions of CH_2CL_2 were made to extract triplicate solutions of the acids spiked into salted water at the 50 ug/l level. The pH of the waters was adjusted to 1-2 prior to extraction. The results of these tests are shown in Table 33.

TABLE 33. EXTRACTION OF THE ACIDIC COMPOUND BY METHYLENE CHLORIDE

	Percent Extracted			
	A	B	C	Average
Quinaldic Acid	0	0	0	0
Trimesic Acid	0	0	0	0
Stearic Acid	105	76.2	97.6	92.9

In conclusion, only stearic acid is effectively extracted from water under the conditions given.

The extraction efficiency for the phenolic compounds was also studied. The procedure was identical to that used previously for the acids (i.e. salted water was adjusted to pH <2 and extracted with 3 x 100 ml portions of CH_2CL_2). Results for these tests are shown in Table 34.

TABLE 34. EXTRACTION OF PHENOLIC COMPOUNDS BY METHYLENE CHLORIDE

	Percent Extracted			
	A	B	C	Average
2,6-di-tert-butyl-4-methylphenol	69.0	63.0	66.5	66.2
2,4-dichlorophenol	92.9	91.7	94.0	92.9

A later resin experiment (also at 120-150 B.V./hour) was performed in which, after passage of 1 liter of spiked salted waters through each of six resins, three of these were desorbed with saturated HCl/Ether and three with saturated HCl/MeOH. The HCl/MeOH eluants gave a brown oily residue after concentration and would not keep a yellow color when diazomethane was added. Thus, it was not possible to analyze these concentrates for the acids.

The HCl/Ether eluants were concentrated and analyzed, however, and the results shown in Table 35 were obtained.

TABLE 35. RECOVERY OF ACIDIC COMPOUNDS IN CONCENTRATED HCl/ETHER ELUANT
Flow Rate: 120-150 B.V./hour

	A	B	C	Average
Quinaldic Acid 49.1 ug/l	16.3	11.0	23.6	16.9
Trimesic Acid 53.9 ug/l	94.4	64.6	100	86.3
Stearic Acid 54.0 ug/l	30.3	20.7	26.4	25.8

A peak corresponding to stearic acid was also found in the resin blank. This gave 2.82 ug, or 5.22%, of the amount spiked into the samples. The origin of this impurity in the blank is unknown. Effluent waters and reservoirs were not analyzed in this experiment. No results were obtained for 2,4-dichlorophenol due to poor derivitization.

The next experiment was conducted at a flow rate of 90 B.V./hour for the adsorption of the carboxylic acids and 2,4-dichlorophenol from water. Lauric acid was also added as a tracer compound. Two sets of triplicates, one with the compounds in salted water and the other with the compounds in deionized water were included in the study. After an initial rinse with ether, the acidic compounds were desorbed with saturated HCl/Ether. Analysis was done by packed column (3% SE-30) after derivatization by diazomethane. The results of these experiments were as summarized in Table 36.

In this experiment, trimesic and quinaldic acids did not esterify well either in standards or samples, and no results could be obtained. Once again, stearic acid was obtained in the resin blank, this time in the amount of 8.8 ug, or 16.3%, of the amount spiked into samples. The source of this contamination is still unknown. Unusually high results were obtained for dichlorophenol and stearic acid on the first sample. However, if these results are treated as outliers, the remaining results are reasonable.

Due to the problems associated with packed column GC analyses, particularly of trimesic and quinaldic acids, the analyses were repeated using capillary GC-FID. It was concluded that these results were more valid, and the results are summarized in Table 37.

TABLE 36. ACIDIC MODEL COMPOUNDS AT 90 BV/HR FLOW (PACKED COLUMN GC)

Model Compounds and Spiking Levels	Percent Recovered Ether/HCl Eluant	Percent In Water	Percent In Reservoir	Mass Balance Percent
	Salted Water			
2,4-Dichlorophenol 49.9 μg/l	48.3	ND	NA	48.3
	65.7	ND	NA	65.7
	78.8	ND	NA	78.8
Stearic Acid 54.1 μg/l	45.3	16.6	NA	61.9
	61.4	6.65	NA	68.1
	113	14.1	NA	127
Lauric Acid 50.2 μg/l	38.8	ND	NA	38.8
	64.7	ND	NA	64.7
	91.8	ND	NA	91.8
	Unsalted (Deionized) Water			
2,4-Dichlorophenol 49.9 μg/l	337*	ND		337*
	84.4	ND		84.4
Stearic Acid	506*	lost		506*
	133	2.40		133
	143	ND		143
Lauric Acid	122	ND		122
	80.5	ND		80.5
	88.9	ND		88.9

ND = Not Detected
NA = Not Applicable
*Outliers

Blanks in this experiment gave peaks (shown in Table 38) corresponding to the amounts of the model compounds based on the origin of 1 liter of water through the column.

TABLE 37. BLANK RESIN EVALUATION FOR ACIDIC COMPOUNDS

	Salted Resin Blank	Unsalted Resin Blank
2,4-dichlorophenol	9.1 ug	8.5 ug
Quinaldic acid	--	--
Trimesic acid	2.8 ug	8.4 ug
Stearic acid	0.8 ug	--
Lauric acid	1.3 ug	2.5 ug

These blanks indicate that more complete cleaning of resin needs to be done prior to each resin experiment.

Several experiments to evaluate the adsorptive capacity of the resin for quinaldic and trimesic acids were then performed. In general, trimesic acid shows less tendency than quinaldic acid to "break-through" the resin. The anions present in the added salts compete with the organic acids for ion-exchange sites and cause earlier "break-through" than would be obtained for deionized water solutions of the organic acids.

The resins used in these adsorption/breakthrough experiments were collected, mixed, and separated into identical portions in order to test and compare the desorption efficiency of various solvents. As a result of these tests, it can be concluded that the desorption capacity for quinaldic acid of the solvents was as follows:

Best	HCl/Methanol
	HCl/Isopropanol
	H_2SO_4/Methanol
	HCl/Ether
	Isopropanol
Worst	Methanol

It was decided to include HCl/Methanol in future desorption schemes in order to improve the recovery of the acids in the concentrate from the resin.

7.6 BREAKTHROUGH/FLOW RATE STUDIES

Since several of the acidic model compounds showed mixed results, it was decided to study the effect of flow rate and the presence of salts by establishing breakthrough curves. Primary emphasis was given to the evaluation of quinaldic acid, both with and without the presence of salts.

TABLE 38. MODEL COMPOUNDS AT 90 B.V./HR FLOW RATE

Model Compounds and Spiking Levels	Salted Water Percent In Ether/HCl Eluant	 Percent In Water	Total Percent Recovered
2,4-Dichlorophenol	9.62	ND	9.62
	50.3	ND	50.3
	10.1	ND	10.1
Quinaldic Acid	13.4	ND	13.4
	48.5	ND	48.5
	20.2	ND	20.2
Stearic Acid	11.7	16.6*	28.3
	40.3	6.65*	47.0
	31.4	14.1*	45.5
Trimesic Acid	37.3	ND	37.3
	78.7	ND	78.7
	38.8	ND	38.8
Lauric Acid	27.3	ND	27.3
	51.8	ND	51.8
	14.9	ND	14.9
	Unsalted (Deionized Water)		
2,4-Dichlorophenol	13.4	ND	13.4
	79.6	ND	79.6
	--	ND	--
Quinaldic Acid	2.24	ND	2.24
	10.2	ND	10.2
	1.83	ND	1.83
Stearic Acid	7.95	lost	7.95
	34.4	2.40*	36.8
	6.28	ND	6.28
Trimesic Acid	13.7	ND	13.7
	36.7	ND	36.7
	8.16	ND	8.16
Lauric Acid	12.4	ND	12.4
	75.3	ND	75.3
	--	ND	--

*Results obtained from packed column GC analysis. (Section 6.10)
All other results obtained by GC/FID analysis (Section 6.3).
N. D. = Not determined

In addition to the acids, other model compounds studied in the adsorption experiments for breakthrough characterization included caffeine, BEHP, furfural, glycine, and anthraquinone.

Model Acidic Compounds on XAD-4 Anionic Resin

A gel permeation chromatography apparatus was adapted for use in pumping and fractionating samples in order to study the adsorption characteristics of the XAD-4 Quaternary resin in the OH^- form. Quinaldic and trimesic acids were selected to be studied first, primarily to determine the effect of salts on the sorption characteristics of the resin for these compounds. The acids were added to the water at approximate levels of 0.25 to 1.83 ppm, which permitted fractions to be analyzed by direct HPLC/UV ion-pair chromatography.

The initial experiments were performed by pumping 1,100 ml of the solutions over the resin at a flow of about 7.0 ml/min, and the effluent collected in 50 ml portions. No breakthrough was observed under these conditions for quinaldic or trimesic acids in either salted or unsalted solutions. Salted solutions were as required in the statement of work (i.e. $CaCl_2$, $CaSO_4$, $NaHCO_3$). The column dimensions were 0.46 cm I.D. with a 6.0 cm height of resin (i.e. 1 cc of wet resin). The flow rate was 405.00 B.V./hour, giving a linear velocity of 40.6 cm/min.

Quinaldic acid in the presence of salts was then studied by passing 2,750 ml of the acid at a concentration of 1.83 mg/l over the resin. The result of this experiment is given by the breakthrough curve in Figure 3. As can be appreciated, breakthrough was at approximately 800-1000 bed volumes, with a subsequent linear increase in concentration. The shape of the curve suggested that the linear velocity was too high for effective adsorption, although some channeling effects in the small column may also have contributed to breakthrough. It was decided to repeat the experiment at a lower velocity.

A linear velocity of 22.0 cm/min was chosen for the next experiment with quinaldic acid. In order to assure that the entire breakthrough curve would be determined, 10 liters of millipore Super-Q water were salted, and quinaldic acid was added at a concentration of 0.988 mg/l. Column dimensions and the amount of resin were the same as in the previous experiment. A total volume of 9,240 ml was passed over the resin, and 23 fractions were collected after wasting the first 500 ml of solution. The results of this experiment are summarized in the breakthrough curve of Figure 4. Initial breakthrough was approximately 1,800 bed volumes, with 50% breakthrough (V_{50}) at about 4,300 bed volumes. Breakthrough still appeared to be influenced by the flow rate and so it was decided to repeat the experiment at a still lower flow rate.

The third experiment in this series for quinaldic acid was performed under the same conditions as described in the previous paragraph, except that a linear flow velocity of 10.3 cm/min was used.

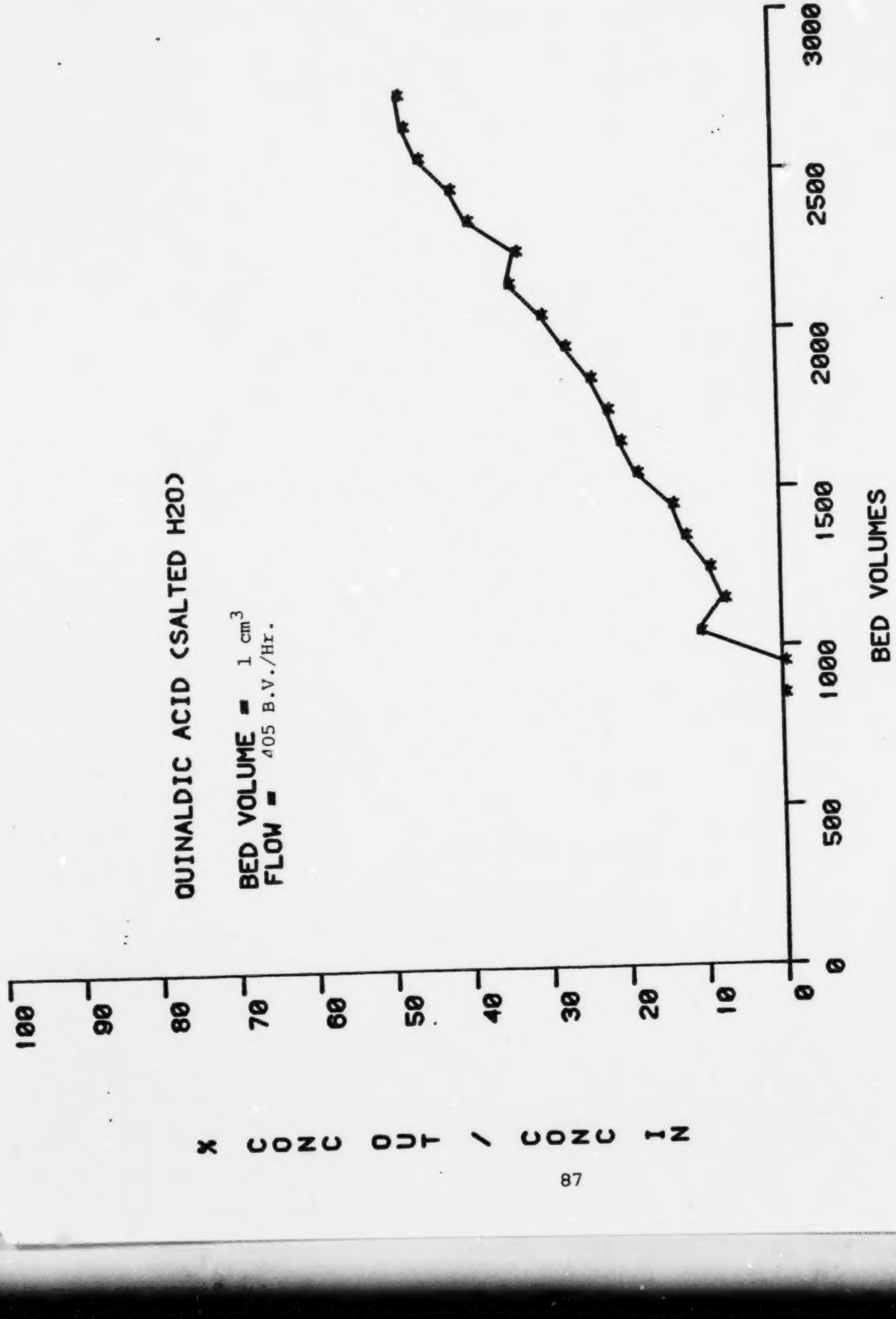

Figure 3. Breakthrough curve - quinaldic acid (linear velocity = 41 cm/min)

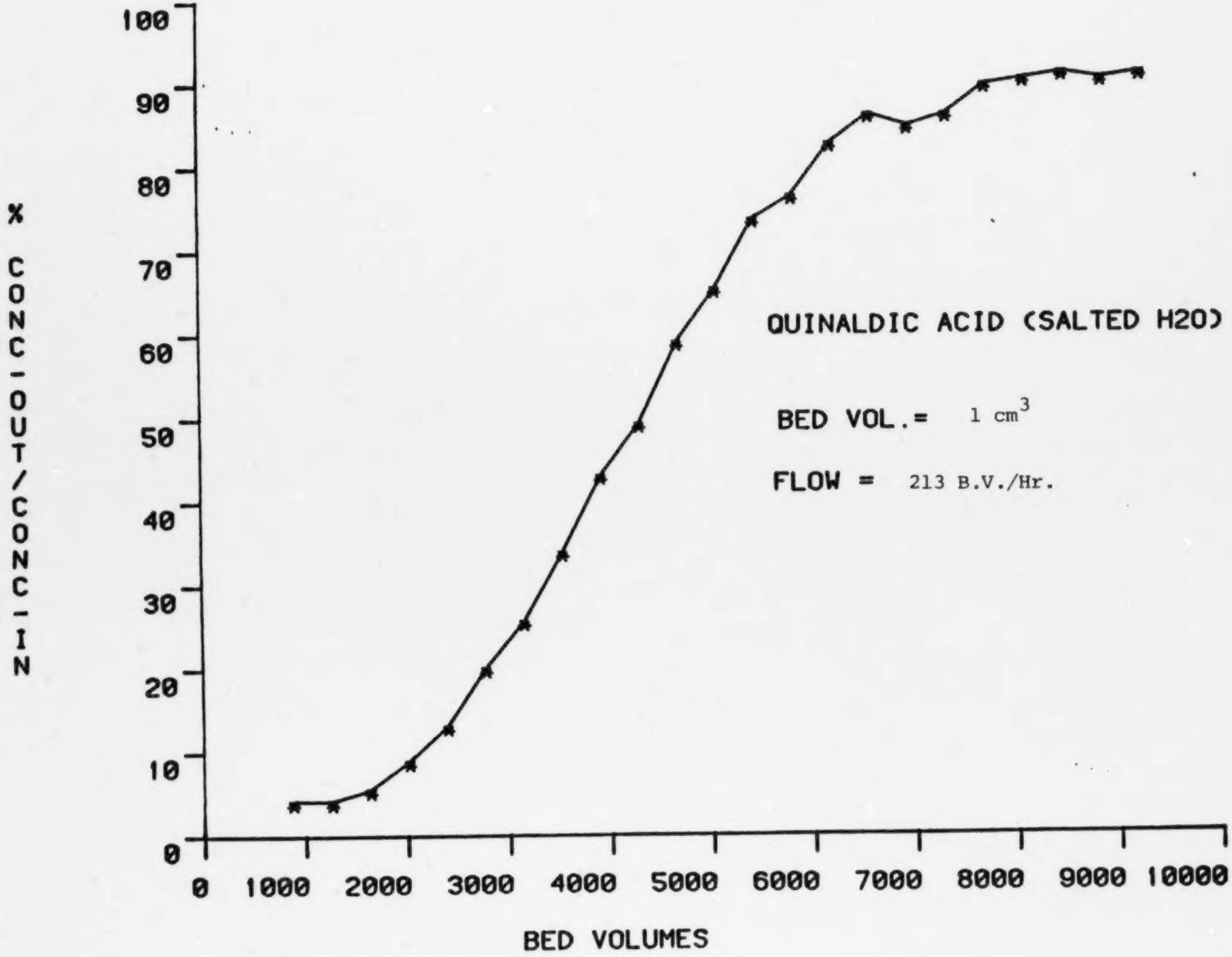

Figure 4. Breakthrough curve - quinaldic acid (linear velocity = 22 cm/min)

The concentration of quinaldic acid was 1.08 mg/l, and a total of 9,200 ml of the solution was passed over the resin. The results of this experiment are summarized in Figure 5. Once again, the slower flow rate gave an improved performance, with initial breakthrough at approximately 2,400 bed volumes and 50% breakthrough (V_{50}) at about 4,700 bed volumes.

For comparative purposes, breakthrough curves for the three different experimental flow rates are summarized in Figure 6. Figure 7 plots the predicted breakthrough curves for 500 liter volumes using the same linear velocities as employed in the three experiments for quinaldic acid.

Figure 7 was based on calculations of experimental data and assuming constant linear velocities, residence times, and flows in bed volumes/hour in scaling up the experimental results to the predicted 500 liter behavior for a 24-hour period. For example, given a linear velocity of 21.0 cm/min, a 17-second residence time, and a flow of 213 bed volumes/hour, then in order to pass 500 liters of water through the resin in 24 hours, the resin bed volume would have to be:

$$\frac{500 \text{ liters}}{24 \text{ hours}} \times \frac{\text{Hour}}{213 \text{ bed volumes}} = 0.0978 \text{ liters}$$

$$\text{or } 97.8 \text{ ml/B.V.}$$

The length of the column is fixed by the residence time, and therefore, the diameter can be calculated as:

$$\frac{d}{2}^{2} h = 97.8 \text{ cc}$$

$$d = \frac{(97.8)\ (4)}{x\ 6}$$

$$d = 4.56 \text{ cm}$$

Similar calculations were made for the other experiments. Finally, the results were plotted in terms of percent breakthrough vs. liters (up to a maximum of 500 liters). These results are considered to be worst case predictions, due to the higher concentrations used and the possibility of channeling having occurred in the small 1 cc experimental column set up.

A final experiment was performed using 10 liters of unsalted water to which had been added quinaldic acid to give a concentration of 0.999 mg/l. Following the same experimental procedure outlined above, no breakthrough was obtained (a flow rate of 3.55 ml/min was used). This clearly indicates that quinaldic acid removal is by an ion-exchange mechanism. Future work, particularly the design of the 500 liters resin experiment, will need to take into account the reduced capacity of the resin for acidic compounds in the presence of salts.

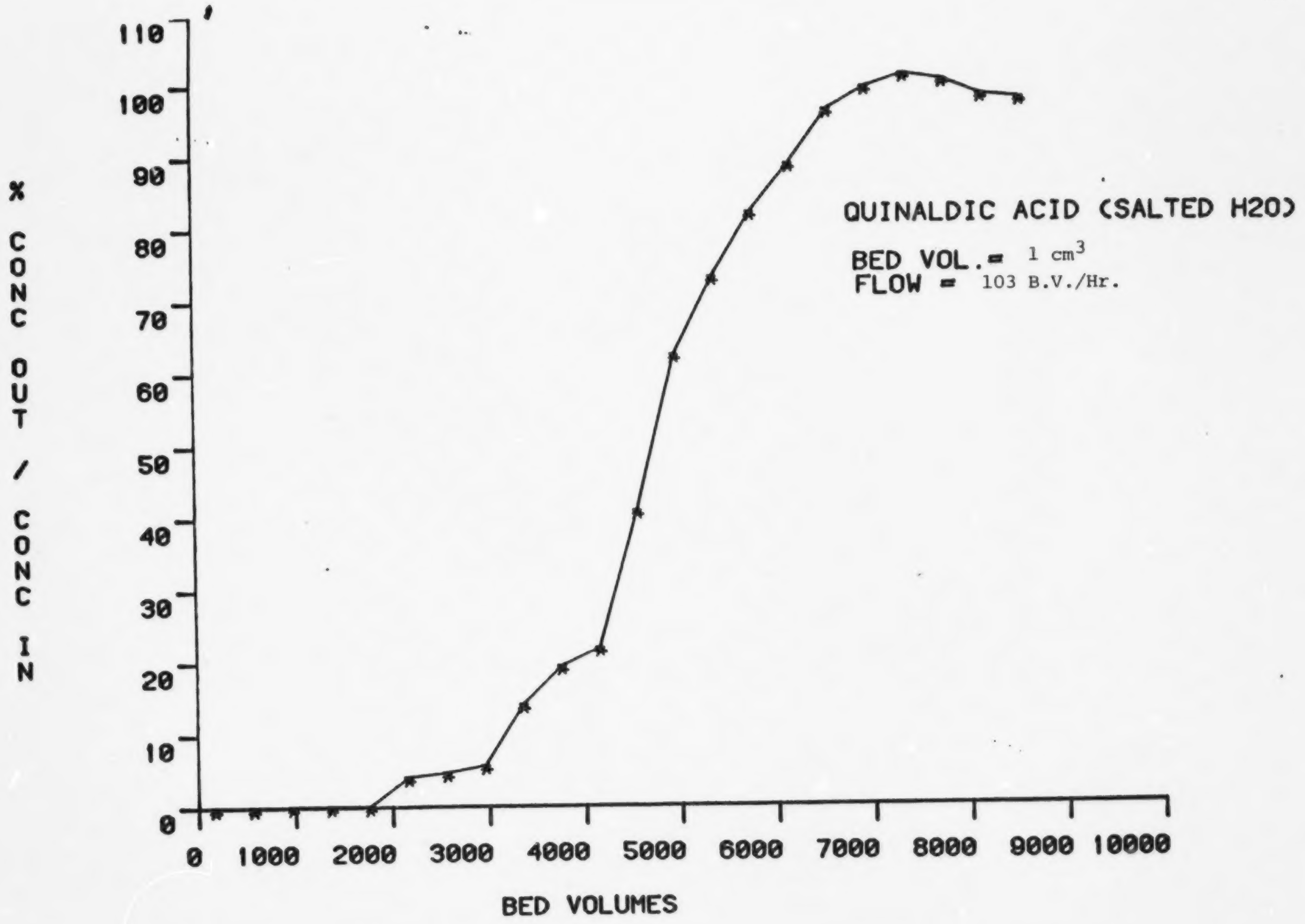

Figure 5. Breakthrough curve - quinaldic acid (linear volocity = 10.3 cm/min)

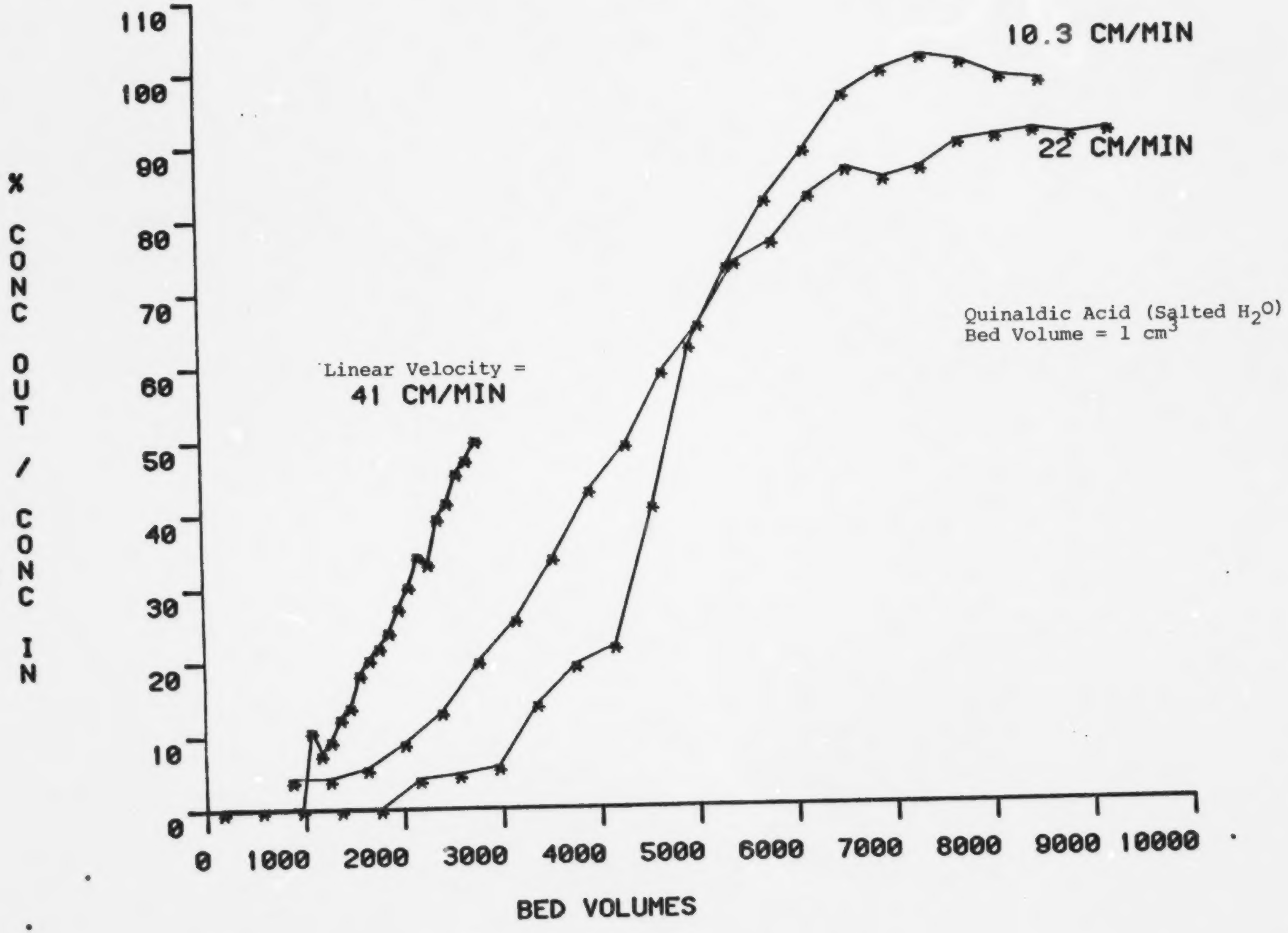

Figure 6. Summary of quinaldic acid breakthrough curves

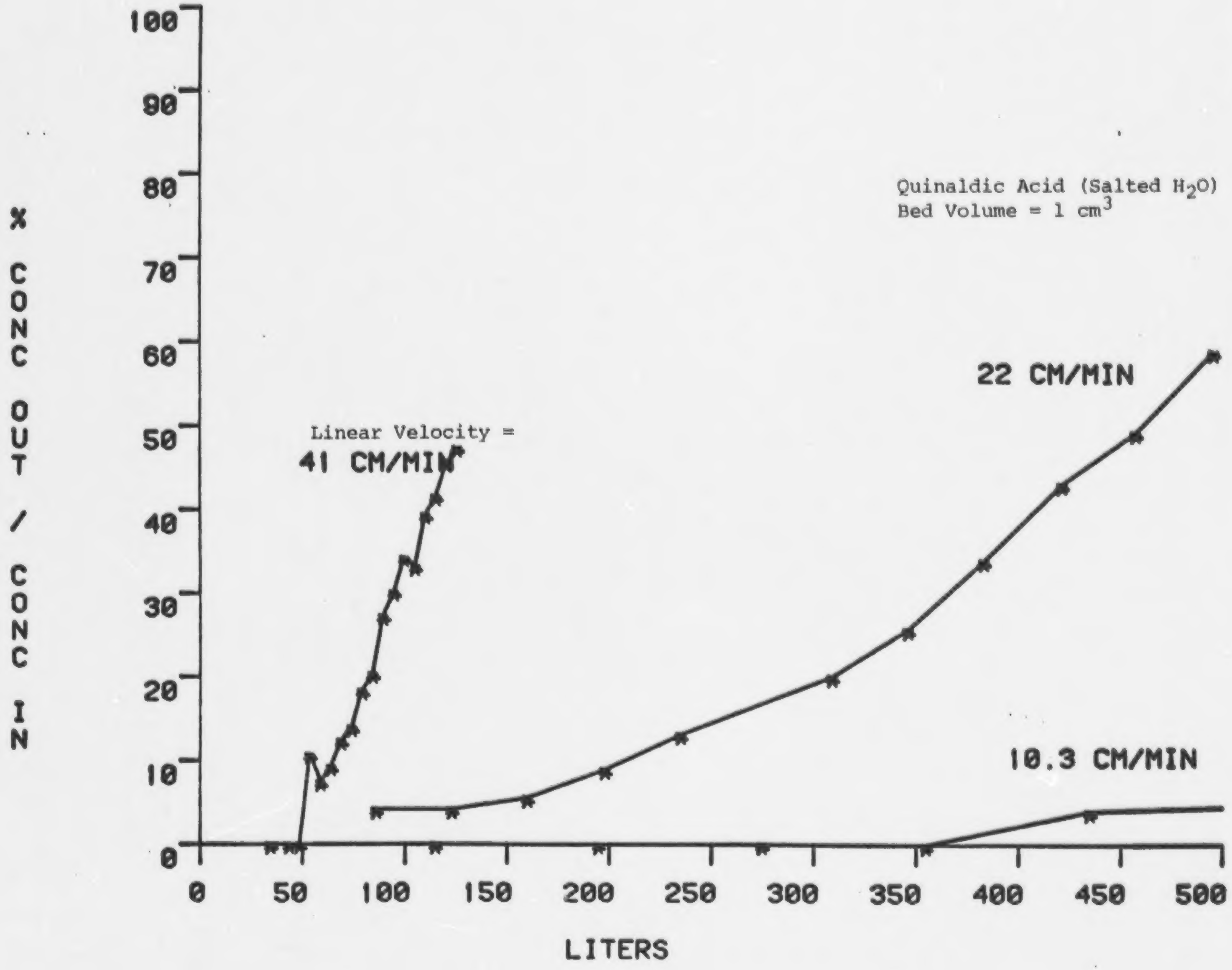

Figure 7. Predicted breakthrough curves for 500 liter volumes (quinaldic acid)

Trimesic acid was also studied for possible breakthrough on XAD-4 anionic resin (OH^- form). Trimesic acid (0.95 mg/l) was added to 2 liters of salted water and passed through 1 cm^3 of wet resin (6.0 cm x 0.46 cm) as in previous experiments. The flow rate was 405 B.V./hour (i.e. 41 cm/min linear velocity). No breakthrough of the trimesic acid was found in this case, although quinaldic acid showed (Figure 3) significant breakthrough under similar conditions. This is probably related to the degree of ionization of the acids under the conditions of the test. Of the acidic model compounds, it appears that quinaldic acid is least favorably adsorbed by the XAD-4 anionic resin. This is the reason it was chosen for in-depth study, and why it also may be useful for estimating the amount of resin required for the scale-up to the 500 liter pilot plant experiments.

Some of the other model compounds were also studied on the XAD-4 anionic resin. Caffeine, furfural, BEHP, and glycine were chosen for further study based on the preliminary 1 liter resin experiments, which indicated that these compounds were present to some degree in aqueous solution after passage through the resin. Anthraquinone, a compound that had shown good resin sorption characteristics in preliminary 1-liter studies, was also included to determine if the adsorption of a typical well adsorbed molecule is affected by the volume of solution passed through the resin. These studies were meant to provide information on compounds which are adsorbed by the resin due to the polymeric nature of the resin (i.e. Van der Waals forces predominate) rather than the ion-exchange mechanism responsible for adsorption of acidic organic compounds.

The first experiment was conducted using the following concentrations of model compounds in water: anthraquinone, 106 ug/l; BEHP, 47 ug/l; caffeine, 765 ug/l; and furfural, 186 ug/l. No haziness was noted after BEHP addition. Conditions for HPLC analyses are listed in Appendices K and L.

Caffeine gave almost immediate breakthrough under the conditions of this test. The results are summarized in Figure 8.

Results for furfural indicated that it had decomposed under the conditions of the test, since it was not present in the input solution at the conclusion of the test.

Anthraquinone did not breakthrough under the conditions of the test, which supports previous conclusions that anthraquinone is effectively concentrated by the resin.

Finally, BEHP was analyzed by GC-ECD (Appendix G) after extracting 5 ml aliquots of solution with 2 ml portions of hexane. Unfortunately, there was scatter in the results and they are inconclusive.

A final experiment in this series was performed, lowering the velocity to 3.6 cm/min, but using the same concentrations of model compounds and analytical conditions as in the previous case.

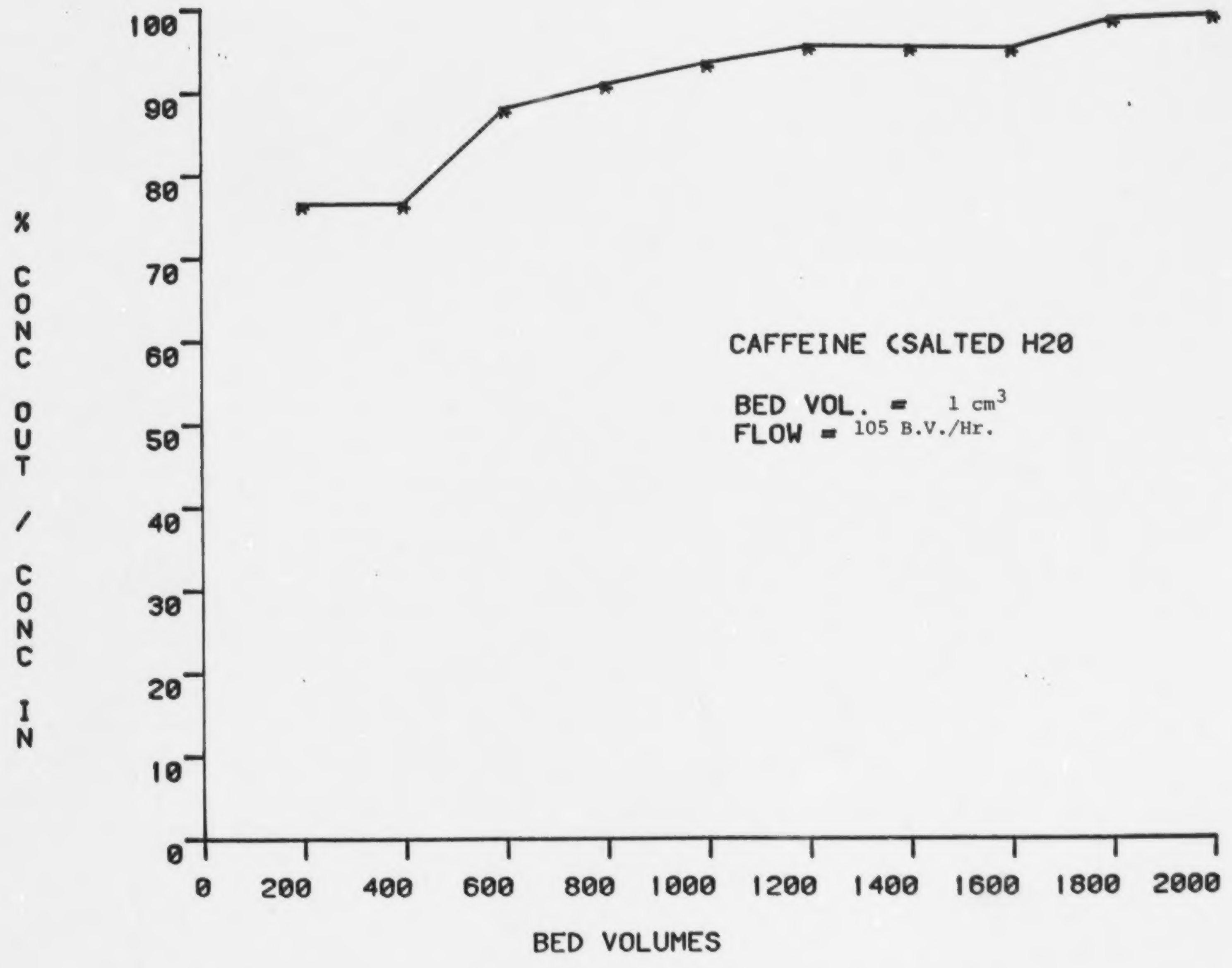

Figure 8. Breakthrough curve - caffeine (flow rate = 105 B.V./Hr.)

The results showed somewhat slower breakthrough of caffeine (See Figure 9). Furfural was not present in the effluent and may have decomposed. BEHP was not analyzed because the extraction and analysis procedure selected proved to be unsatisfactory.

7.7 EFFECTIVENESS OF THE RESIN PROCEDURE IN ISOLATING AND CONCENTRATING HUMIC SUBSTANCES FROM WATER WITHOUT OTHER MODEL COMPOUNDS

This experiment was performed for the purpose of determining the effectiveness of the resin procedure in isolating and concentrating humic substances from water. In this experiment, the humic substances were treated identically to the other model compounds previously evaluated. That is, the experimental design included triplicate samples and a resin blank. Samples contained 2000 ug/l of humic substances plus salts. The resin blank was performed with salted water. As for the other preliminary evaluations of model compounds, the flow rate for these experiments was 120-150 B.V./hour, using 10 cm^3 of resin. One liter portions of samples and blanks were passed through the resin. Elution was as follows:

1) 2 x 25 ml ether
2) 2 x 10 ml MeOH
3) 2 x 25 ml 0.1 N HCl/MeOH
4) 2 x 25 ml saturated HCl/MeOH
5) 10 ml saturated HCl/MeOH

Although it was not anticipated that ether would desorb the humic substances, it was included since a normal desorption scheme would also include it for recovery of neutral compounds. The methanol served the purpose of drying the resin, although it was thought that some humic substances might be desorbed by methanol. The HCl/MeOH solutions were included in the scheme to desorb the acidic model compounds as well as the humic substances, which have both carboxylic acid groups and phenolic groups in their structure. The scheme included initial desorption with 0.1 N HCl/MeOH, since it was believed that the strength of HCl was sufficiently strong to achieve the desorption of the lower molecular weight acids, while preliminary tests showed that saturated HCl/MeOH would be necessary to achieve significant desorption of the humic substances. The saturated HCl/MeOH eluants were separated into 2 portions, one of 50 ml and a final of 10 ml. The final 10 ml portion was added to determine if the humic substances were still being desorbed at that stage.

Analysis of the eluants was performed by visible spectrophotometry, using a wavelength of 330 nm (Section 6.7). Figures 10 and 11 present calibration curves for standard solutions of humic substances in 0.1 N HCl/MeOH and saturated HCl/MeOH, respectively. Results for this experiment are presented in Table 39.

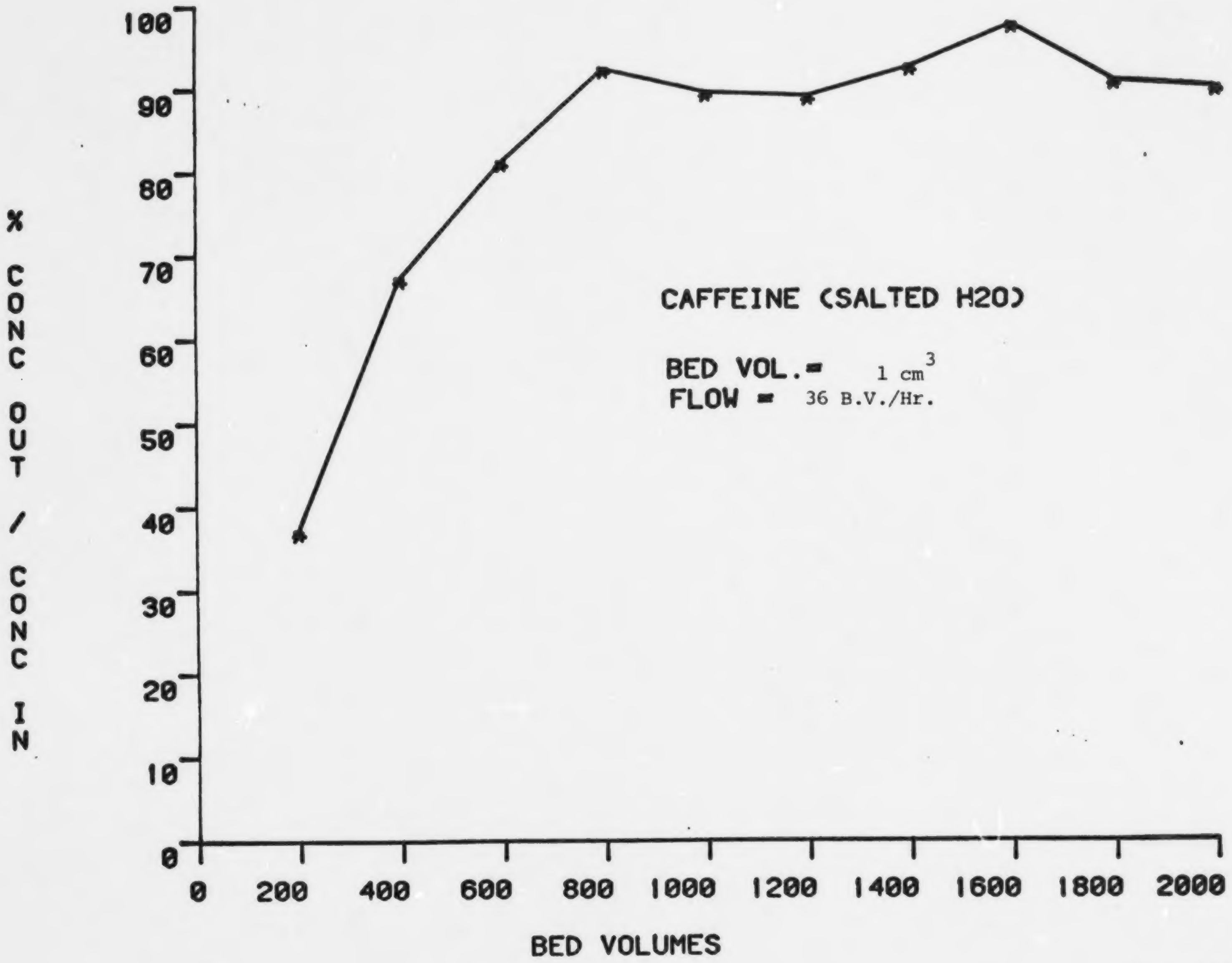

Figure 9. Breakthrough curve - caffeine (flow rate = 36 B.V./Hr.)

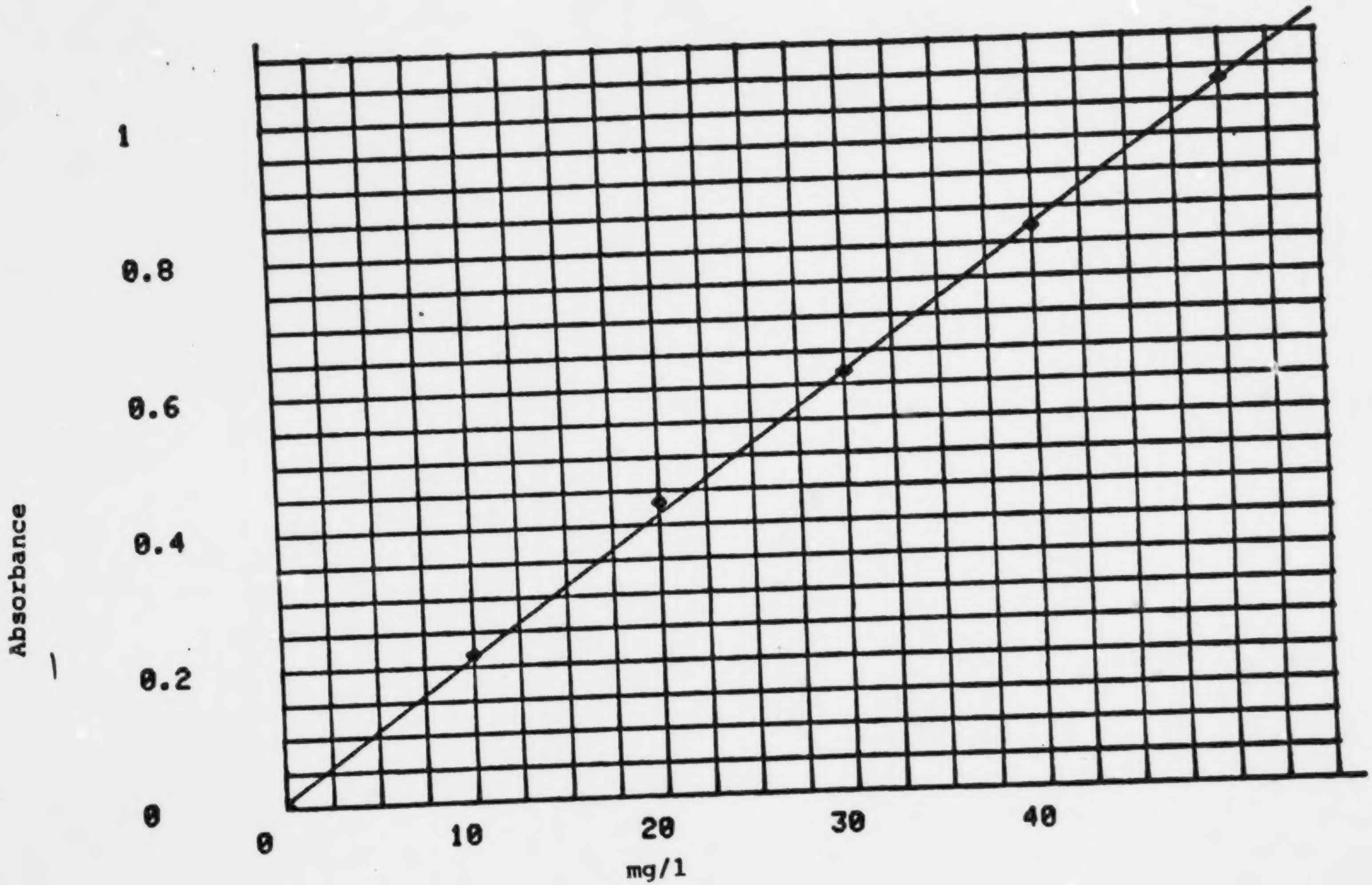

Figure 10. Humic substances in 0.1N HCl/methanol (λ= 330nm)

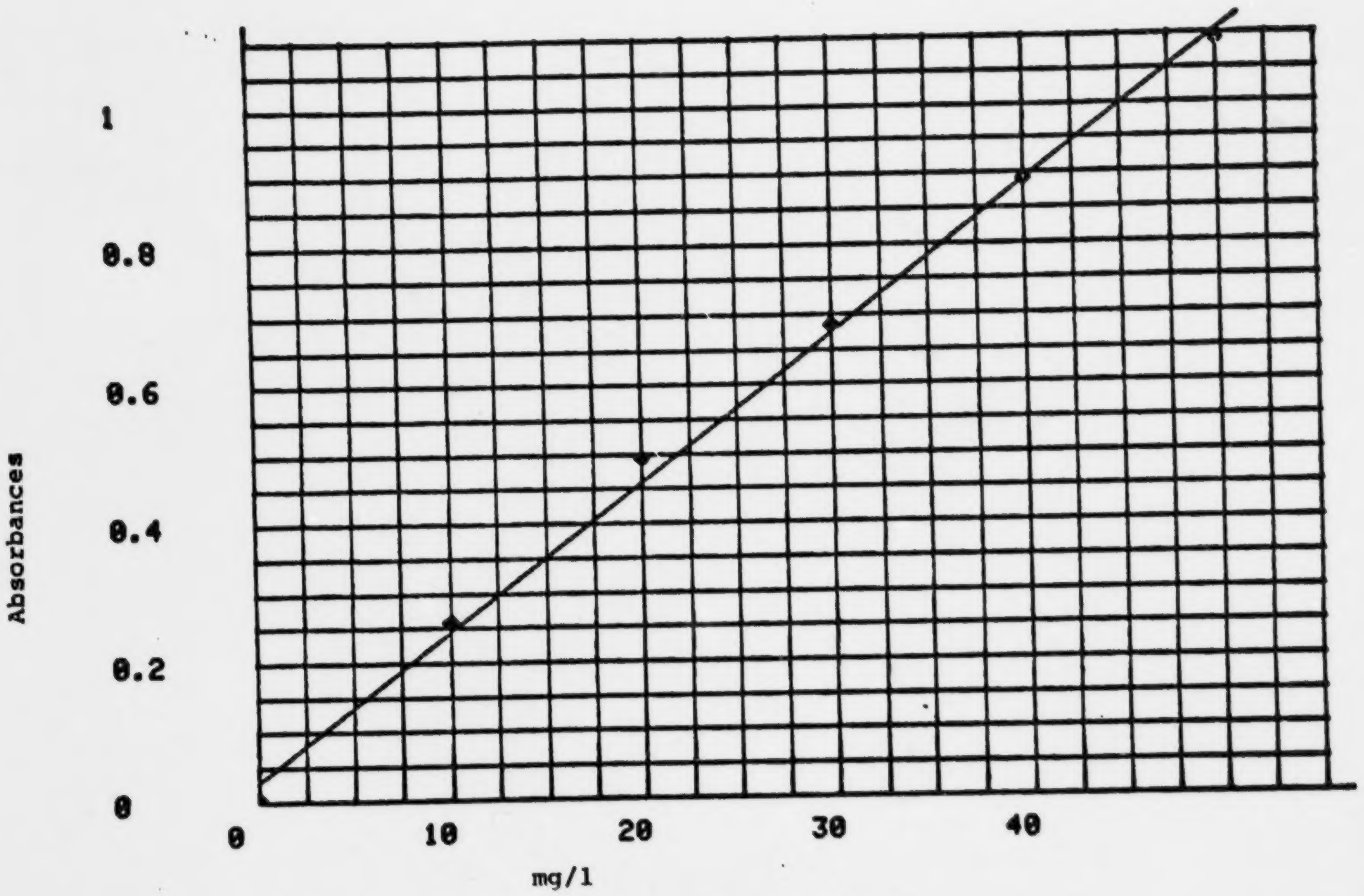

Figure 11. Humic substances in saturated HCl/MeOH (λ = 330 nm)

TABLE 39. MASS BALANCE FOR CONCENTRATION OF HUMIC SUBSTANCES USING XAD-4 ANIONIC RESIN

	Micrograms of Humic Substances in 0.1 N HCl/MeOH	Micrograms of Humic Substances in 1st 50 ml of Saturated HCl/MeOH	Micrograms of Humic Substances in Final 10 ml of Saturated HCl/MeOH	Total Micrograms and Percent of Humic Substances Recovered
Sample A	595	889	123	1607, 80.4 percent
Sample B	630	838	145	1613, 80.7 percent
Sample C	644	793	135	1572, 78.6 percent
Resin Blank	0	40.5	10.4	---

From these results, it can be seen that the total recovery of humic substances from the resin is comparable to those obtained for other model compounds. In order to achieve this, however, concentrated HCl/MeOH eluants are needed. Two of the blanks gave responses in the analysis for humic substances. The significance of these blank values is not clear, however, since the detection limit of the spectrophotometric methods has not been determined.

7.8 CONCENTRATION OF MODEL COMPOUNDS IN THE PRESENCE OF HUMIC SUBSTANCES AT 48 B.V./HOUR FLOW RATE

As previously mentioned in discussions of breakthrough experiments of quinaldic acid, a lower adsorption flow rate of 48 B.V./hour showed to be more favorable than 120-150 B.V./hour. Therefore, two experiments were undertaken. The primary purpose was to determine if the presence of humic substances had any effect on the concentration of the other model compounds. The secondary purpose of these experiments was to evaluate the concentration technique with all model compounds present at a lower flow rate of 48 B.V./hour.

In the first experiment, the model compounds were added to pure water at the levels specified in the statement of work (Table 1). Salts were added at the specified levels.

The experimental design included 3 resin columns used to concentrate the model compounds in the absence of humic substances, and one resin column used to concentrate the model compounds in the presence of humic substances. The recovery of the model compounds in the presence of humic substances was compared with the 95% confidence interval of results from triplicate runs without humic substances in order to judge whether the humic substances interfered significantly with the concentration of the model compounds. It was appreciated that analytical interference might also be present, but this problem was only to be addressed if the results for model compounds in the presence of humic substances were found to be outside the expected 95% confidence interval range.

It was decided to only analyze for selected neutral organic model compounds in this experiment, in order to simplify the analytical work. The remaining model compounds were analyzed in the second experiment using identical conditions for adsorption and desorption. Since only neutral compounds were analyzed, ether was the only eluant required. Three 20 ml portions of freshly distilled ether were used for elution. Reservoirs were rinsed with 2-20 ml portions of ether. Effluent waters were extracted with 3-100 ml portions of methylene chloride at both pH 11 and pH 2.

Quality control was limited in this experiment to a reagent blank and to resin blanks done both with and without humic substances. The purpose of the reagent blank was to determine whether any analytical interferences were contributed by the reagents. The purpose of the resin blanks was to determine whether any analytical interferences were contributed either by the resin or by the humic substances.

Analyses were done by capillary GC-FID, using pentadecane as an internal standard (Section 6.3). Results for this experiment are summarized in Table 40. In most cases, there was no evidence that the humic substances affected the concentration of the model compounds included in this experiment. The result for 1-chlorododecane in the presence of humic substances was outside the 95% confidence interval as determined by a triplicate run in the absence of humic substances. This may be a real effect, but the narrow confidence interval found for triplicate runs may not be a good estimate of the true 95% confidence interval. Also, 1-chlorododecane is a somewhat volatile compound, and this fact may contribute to the existence of outliers. The result for bis(2-ethylhexyl)phthalate was also lower in the presence of humic substances than one might expect from the 95% confidence interval estimate. Note that 2,6-di-tert-butyl-4-methylphenol was just barely within the acceptable 95% confidence interval limit. Finally, it should be mentioned that furfural was included in this experiment, but one of the samples in the absence of humic substances and one of the samples in the presence of humic substances gave zero recovery. Thus, no conclusions regarding furfural could be reached.

The second experiment provided an opportunity to evaluate whether the interactions of the model compounds affected their behavior during concentration with humic substances. This experiment was also performed at the lower flow rate of 48 B.V./hour.

All model compounds were added at the specified concentration as shown in Table 1. An attempt was made to perform analyses for all model compounds and to make mass balances. This was not entirely possible as can be seen from the data.

The basic experimental design and procedures for this experiment were the same as those used previously (Appendix M). The desorption scheme and the analytical scheme were both more complicated in this experiment due to the fact that all model compounds were to be evaluated. Desorption was as follows:

1) Distilled ether, 6 x 25 ml

2) Methanol, 2 x 25 ml

3) 0.1 N HCl/methanol, 2 x 25 ml

4) Saturated HCl/methanol, 2 x 25 ml, or until all humic material desorbed as indicated by color

The ether was to desorb the neutral organic compounds. Methanol was to desorb any neutral compounds not entirely desorbed by ether, such as caffeine. The 0.1 N HCl/methanol was to desorb the acidic model compounds. Finally, the saturated HCl/methanol was intended to desorb the humic substances.

The analytical scheme was complicated by several factors. Firstly, it was designed to provide for mass balance of the model compounds. Secondly, it was known that some compounds, such as the

TABLE 40. EVALUATION OF THE EFFECT OF THE HUMIC SUBSTANCES ON THE CONCENTRATION OF MODEL COMPOUNDS WITH XAD-4 ANIONIC RESIN (48 BV/HR FLOW RATE)

		Recovery from Eluant in Absence of Humic Substances			
Model Compounds	N	Mean Percent Recovery	Standard Deviation	95% Confidence Interval	Percent Recovery from Eluant in Presence of Humic Substances
methyl isobutyl ketone	3	51.7	16.5	51.7 ± 41.0	52.3
furfural	2	44.2	7.92	--	--
isophorone	3	58.9	9.65	58.9 ± 24.0	58.1
quinoline	3	90.2	2.03	90.2 ± 5.0	89.8
biphenyl	3	81.8	1.47	81.8 ± 3.7	82.3
1-chlorododecane	3	63.9	1.89	63.9 ± 4.7	51.0
2,6-di-tert-butyl-4-methylphenol	3	33.3	5.31	33.3 ± 13.2	20.4
2,4'-dichlorobiphenyl	3	102	4.95	102 ± 12.3	102
phenanthrene	3	114	4.58	114 ± 11.4	112
caffeine	3	43.9	2.93	43.9 ± 7.3	41.4
2,2',5,5'-tetrachlorobiphenyl	3	108	5.20	108 ± 12.9	105
anthraquinone	3	99.0	8.13	99.0 ± 20.2	89.8
bis(2-ethylhexyl) phthalate	3	82.3	11.1	82.3 ± 27.6	58.7

acids, were not easily quantified, and thus as a conservative measure, these compounds were analyzed by more than one technique. Refer to Section 6 for the grouping of the compounds for analytical purposes.

In summary, the analytical scheme was as follows:

Ether Reservoir Rinse (2 x 20 ml distilled ether) - Freeze out water. Measure the volume of the decanted ether. Remove the following aliquots:

5 ml for 5-chlorouracil analysis (HPLC)
5 ml for quinaldic and trimesic acids (HPLC)
5 ml for quinaldic, trimesic and stearic acids and 5-chlorouracil (GC/FID capillary)
5 ml for humics analysis
1 ml for chloroform by GC/EC

Concentrate the remainder to 1.0 ml and spike with 5 ug internal standard. Analyze for all Group I compounds by capillary GC/FID.

Ether Eluant (6 x 25 ml) - Freeze out water. Measure the volume and remove 1 ml for analysis of chloroform. Concentrate the remainder to 1 ml and spike with 10 ug of internal standard. Analyze for all Group I compounds by capillary GC/FID.

Methanol Eluant (2 x 25 ml) - Measure the volume and remove 5 ml for humics analyses. Concentrate the remainder to dryness and solvent exchange to methylene chloride to a final volume of 1.0 ml; spike with 20 ug of internal standard. Analyze this fraction by GC/FID capillary for all Group I compounds with special emphasis on caffeine.

0.1 N HCl/Methanol (2 x 25 ml) - Measure the volume and remove aliquots for the following analyses:

5-chlorouracil by HPLC
Quinaldic and trimesic acids by HPLC
Humic substances by visible spectrophotometry
2,4-dichlorophenol by capillary GC/FID (after dilution with water, 2,4-dichlorophenol in acid form is extracted with 3 x25 ml of CH_2Cl_2, then concentrated to 1.0 ml and 20 ug internal standard added prior to gas chromatographic determination)

Concentrate the remaining volume to near dryness on a water bath. Add several milliliters of distilled ether, concentrate to near dryness, and repeat four or five more times to remove HCl. Esterify with diazomethane and analyze by capillary GC/FID for Group II compounds. It is noteworthy that 5-chlorouracil also gave a derivative with diazomethane. Retain all concentrate after GC/FID analysis for possible HPLC analysis.

Saturated HCl/Methanol - Measure the volume of water, adjust the pH to $\geq$11, extract with 3 x 100 ml CH_2Cl_2; adjust the pH to $\geq$2, extract with 3 x 100 ml CH_2Cl_2. Measure the volume of CH_2Cl_2 extract. Remove 1 ml for GC/ECD analysis of chloroform. Concentrate the remainder of CH_2Cl_2 extracts separately to a final volume of 1.0 ml; spike with 5 ug of internal standard. Analyze the basic extract for all Group I compounds by capillary GC/FID. Analyze the acidic fraction for stearic acid and 2,4-dichlorophenol by capillary GC/FID also.

Experimental Results

With respect to the effect of humic substances on the concentration of Group I model compounds, the results of this experiment are summarized in Tables 41 and 42.

These results substantially confirm those obtained and reported previously for the neutral model compounds. However, MIBK was not recovered this time, indicating that the volatile nature of this compound can cause erratic results. While MIBK is almost certainly present in the ether eluant, subsequent Kuderna-Danish concentration can result in its loss. Furfural was not recovered at all, thus showing even more erratic behavior than obtained previously for this compound. Results for biphenyl and 1-chlorododecane showed some possible difference between recovery in the presence and absence of humic substances, but this may be due to the narrow confidence intervals resulting from the excellent precision in analyses of the triplicate runs in the absence of humic substances. The previous experiment showed no effect of humic substances for the recovery of biphenyl. However, 1-chlorododecane did show slightly low recovery in both experiments, so some slight effect of humic substances is indicated.

Table 42 indicates that two compounds, caffeine and anthraquinone, were found in the methanol eluants. The amount of anthraquinone was almost negligible, while a significant amount of caffeine was present. No effect of humic substances on recovery was apparent from the results.

Table 43 summarizes the results for concentration of the acidic model compounds by 0.1 N HCl/methanol eluant. As expected, the analyses of these acidic compounds proved difficult, and some alterations in planned analyses were necessary. The quantitative results for the compounds listed in Table 43 were obtained using the following analytical techniques:

Compound	Analytical Technique for Quantitation	
Quinaldic acid	Section 6.4	HPLC
Trimesic acid	Section 6.4	HPLC
Stearic acid	Section 6.3	Capillary GC/FID of methyl ester (diazomethane dederivatization)
2,4-dichlorophenol	Sections 6.3 & 6.8	GC/FID (also GC/MS)
5-chlorouracil	Section 6.5	HPLC

TABLE 41. EVALUATION OF THE EFFECT OF THE HUMIC SUBSTANCES ON THE CONCENTRATION OF GROUP I (NEUTRAL) MODEL COMPOUNDS WITH XAD-4 ANIONIC RESIN (ETHER ELUANT) (48 BV/HR FLOW RATE)

	Recovery from Ether Eluant in Absence of Humic Substances				
Model Compounds	N	Mean Percent Recovery	Percent Standard Deviation	95% Confidence Interval	Percent Recovery from Ether Eluant in Presence of Humic Substances
methyl isobutyl ketone	Not recovered				
furfural	Not recovered				
isophorone	3	98.2	6.82	98.2 ± 16.9	93.4
quinoline	3	96.3	6.20	96.3 ± 15.4	90.2
biphenyl	3	99.1	3.00	99.1 ± 7.4	89.6
1-chlorododecane	3	78.2	1.74	78.2 ± 4.33	70.8
2,6-di-tert-butyl-4-methylphenol	3	67.5	15.2	67.5 ± 37.7	66.0
2,4'-dichlorobiphenyl	3	82.1	2.52	82.1 ± 6.3	78.0
phenanthrene	3	72.8	5.59	72.8 ± 13.9	75.1
caffeine	3	52.2	9.39	52.2 ± 23.3	44.4
2,2'-5,5'-tetrachlorobiphenyl	3	104	14.1	104 ± 34.9	108
anthraquinone	3	68.4	8.31	68.4 ± 20.6	71.0
bis(2-ethylhexyl) phthalate	3	53.8	10.4	53.8 ± 25.8	55.6
chloroform	3	132	26.7	132 ± 66.2	116

TABLE 42. EVALUATION OF THE EFFECT OF THE HUMIC SUBSTANCES ON THE CONCENTRATION OF GROUP I (NEUTRAL) MODEL COMPOUNDS WITH XAD-4 ANIONIC RESIN (METHANOL ELUANT)

(48 BV/HR FLOW RATE)

		Recovery from Methanol Eluant in Absence of Humic Substances			
Model Compounds	N	Mean Percent Recovery	Standard Deviation	95% Confidence Interval	Percent Recovery from Eluant in Presence of Humic Substances
Caffeine	3	9.83	1.40	9.82 ± 3.48	9.18
Anthraquinone	3	0.47	0.15	0.47 ± 0.37	0.54

NOTE: BEHP was also found in the methanol eluants from the resins both in absence and presence of humic substances. However, the amount present was of the same order of magnitude as that in the reagent and resin blanks, and therefore, not considered significant. No other model compounds were found in the methanol eluants.

TABLE 43. EVALUATION OF THE EFFECT OF THE HUMIC SUBSTANCES ON THE CONCENTRATION OF GROUP II (ACIDIC) MODEL COMPOUNDS WITH XAD-4 ANIONIC RESIN (0.1 N HCl/METHANOL) (48 BV/HR FLOW RATE)

	Recovery from 0.1 N HCl/Methanol Eluant in Absence of Humic Substances			
Model Compounds	Mean Percent Recovery	Standard Deviation	95% Confidence Interval	Percent Recovery from 0.1 N HCl/Methanol Eluant in Presence of Humic Substances
Stearic Acid	Not Recovered			
Quinaldic Acid	81.3	9.75	81.3 ± 24.2	76.8
Trimesic Acid	Not Recovered			
2,4-dichlorophenol	100	4.97	100 ± 12.3	133
5-chlorouracil	Not Recovered			

The analysis of 2,4-dichlorophenol by GC/MS provided some unexpected information. It was found that benzoic acid was also present, and it appears that the benzoic acid is an artifact eluted from the resin by 0.1 N HCl/methanol. The GC/MS analysis was necessary because the peak from the benzoic acid interfered in the analysis of 2,4-dichlorophenol by capillary GC/FID. As indicated previously, the 0.1 N HCl/methanol eluants were diluted and extracted with CH_2Cl_2 to isolate the 2,4-dichlorophenol. This procedure also provided a way to isolate extractable artifacts from the acidic eluants, a task that had eluded us previously. The following amounts (micrograms) of benzoic acid were found in the experiment.

Samples			Resin	Reagent
A	B	C	Blank	Blank
175 ug	415 ug	320 ug	514 ug	2.4 ug

The low value of benzoic acid in the reagent blank and the high value in the resin blank provides conclusive evidence that benzoic acid is an artifact.

Finally, Tables 44 and 45 summarize mass balance data for the model compounds included in this experiment. Table 44 includes Group I compounds plus glycine from Group III. It was not possible to analyze for glucose, but it is almost certain that glucose remained in the water and was not concentrated. Results for neutral organic compounds were generally similar to those obtained previously. Chloroform recoveries were greater than 100%, and were attributed to background contamination of chloroform in the reagents used (i.e. water and ether as indicated in the resin blank and reagent blank.

For glycine, the measurements of percent recovery in water (Table 44) did not include any blank correction for other fluorescing model compounds in water. This was because measurements showed that the background fluorescence of model compounds was the same both before and after passing solutions of these compounds through the resin.

TABLE 44. MASS BALANCE SUMMARY FOR GROUP I (NEUTRAL ORGANICS) AND GLYCINE

Humic Substances = Absent · Salts = Present Conc. = As in Table 1

		% Recovered From Ether Eluant	% Recovered From Methanol Eluant	% Recovered From Water*	% Recovered From Reservoir Rinse	Total Percent Recovered
Isophorone	A	104	ND	1.02	ND	105
	B	100	ND	ND	ND	100
	C	90.6	ND	ND	ND	90.6
Quinoline	A	103	ND	ND	ND	103
	B	96.2	ND	ND	ND	96.2
	C	90.2	ND	ND	ND	90.2
Biphenyl	A	103	ND	ND	ND	103
	B	97.2	ND	ND	ND	97.2
	C	97.6	ND	ND	ND	97.6
1-chlorododecane	A	76.2	ND	ND	ND	76.2
	B	79.0	ND	ND	ND	79.0
	C	79.4	ND	ND	ND	79.4
2,6-di-tert-butyl-4-methylphenol	A	77.2	ND	ND	ND	77.2
	B	50.0	ND	ND	ND	50.0
	C	75.4	ND	ND	ND	75.4
2,4-dichlorobiphenyl	A	82.4	ND	ND	ND	82.4
	B	84.4	ND	ND	ND	84.4
	C	79.4	ND	ND	ND	79.4
Phenanthrene	A	75.6	ND	ND	ND	75.6
	B	76.5	ND	ND	ND	76.5
	C	66.4	ND	ND	ND	66.4

(Continued)

TABLE 44. (Continued)

Caffeine	A	58.4	10.4	4.08	ND	72.8
	B	56.8	10.9	2.25	ND	70.0
	C	41.4	8.24	2.67	ND	52.3
2,2',5,5'-tetrachlorobiphenyl	A	117	ND	ND	ND	117
	B	106	ND	ND	ND	106
	C	89.4	ND	ND	ND	89.4
Anthraquinone	A	73.2	0.78	0.90	ND	74.9
	B	73.2	--	--	ND	73.2
	C	58.8	0.98	--	ND	59.8
Bis(2-ethylhexyl) phthalate	A	59.0	1.84	7.35	ND	68.2
	B	60.6	1.88	7.61	ND	70.1
	C	41.8	3.80	11.4	ND	57.0
Chloroform	A	123	NA	9.42	23.8	156
	B	111	NA	3.78	31.4	146
	C	162	NA	13.3	11.1	186
Methyl isobutyl ketone	A	ND	ND	ND	ND	0
	B	ND	ND	1.22	ND	1.22
	C	ND	ND	ND	ND	0
Furfural	A	ND	ND	34.9	ND	34.9
	B	ND	ND	31.3	ND	31.3
	C	ND	ND	33.2	ND	33.2
Glycine	A	NA	NA	101	NA	101
	B	NA	NA	93.1	NA	93.1

*Values have been corrected for extraction efficiency.

TABLE 45. MASS BALANCE FOR GROUP II (ACIDIC) COMPOUNDS

Humic Substances = Absent Salts = Present Conc. = As in Table 1

Model Compounds		Percent Recovered From 0.1 N HCl/Methanol Eluant	Percent Recovered From Water	Percent Recovered From Reservoir	Total Percent Recovered
Stearic Acid	A	--	18.7	ND	18.7
	B	--	16.6	ND	16.6
	C	--	15.6	ND	15.6
Quinaldic Acid	A	92.4	NA	ND	92.4
	B	74.0	NA	ND	74.0
	C	77.6	NA	NA	77.6
Trimesic Acid	A	--	NA	NA	0
	B	--	NA	NA	0
	C	--	NA	NA	0
2,4-dichlorophenol	A	106	ND	ND	106
	B	96.4	ND	ND	96.4
	C	99.0	ND	ND	99.0
5-chlorouracil	A	--	NA	ND	0
	B	--	NA	ND	0
	C	--	NA	ND	0

SECTION 8

PILOT PLANT DESIGN, EXPERIMENTS AND RESULTS

Design of the pilot plant scale-up was based upon the earlier study involving quinaldic acid breakthrough. Since this compound may represent a "worst case", other factors must be considered.

The inside diameter and length of the resin bed was determined by considering the following two factors:

1) Residence time

2) Bed volume per unit time or/through-put

It was decided to keep these two factors as close as possible during scale-up from bench scale studies to the pilot plant studies. The first factor controls the rate of adsorption, and the through-put controls the capacity of the XAD-4 Quaternary resin.

The breakthrough studies on quinaldic acid can be summarized as follows:

Flow (ml/min)	Velocity (cm/min)	Residence Time (seconds)	Bed Volume/Hr
6.75	40.6	9	405
3.66	22.0	16.4	220
1.72	10.3	35.0	103

Figure 10 shows that at 10% breakthrough, the bed volume is approximately 3200 ml. The project requirement for sampling was 500 liters of water to be concentrated during a 24 hour period. Therefore, the following calculations would result in the amount of resin needed:

Flow - 1.72 ml/min
B.V./hr = 1.72 x 60 = 103
103 B.V./hr x 24 =2472 BV
500 liters/2472 ≈0.2 liters resin

The above calculation shows that the bed volume of about 2500 ml found is close to the bed volume of 3200 ml in the breakthrough study of quinaldic acid.

Since the volume of the resin required has been established (to handle 103 B.V./hr) the inside diameter (D) and the length (L) of the bed can be determined which would be comparable to the residence time of the guinaldic breakthrough study. Two approaches can be followed in length and diameter determination. One involves duplicating the breakthrough or the bench-scale studies. The second approach involves the practical aspects such as L/D ratio and the pressure drop phenomenon. As a general rule, the L/D should be more than or equal to 10. Therefore, a 16 inches length by 1.0 inch inside diameter column was 10. Therefore, a 16 inches length by 1.0 inch inside diameter column was constructed with the following characteristics:

Surface area = 4.9 cm^2
Residence time = 0.57 min
Bed volume/hr = 103
Flow rate = 347 ml/min
Linear velocity = 70.8 cm/min
L/D = 16

A total of 4 pilot plant studies were performed:

	Resin Blank	1	2	3
Salts	present	present	absent	present
Model compounds	absent	present	present	present
Humic substances	absent	absent	absent	present

8.1 RESIN BLANK PILOT STUDY

The procedure for the resin blank pilot study was designed to be exactly the same as for studies with model compounds. Two basic types of analyses were performed. The eluants were analyzed by GC/MS (after concentration) for the purpose of identifying and estimating the artifacts in the resin. Reagent blanks were also analyzed simultaneously for comparative purposes. The second type of analysis was performed by the same procedures proposed for the model compound pilot plant studies. The purpose of variations in the analyses was to determine whether any interferences from the resin would affect the results for model compound analyses.

The procedure for the resin blank pilot plant runs can be summarized as follows:

1) Fill reservoir with 500 lt organic free deionized water and add salts; measure pH, and adjust to 7.0, if necessary.

2) Take 50 ml aliquot for chloroform analysis.

3) Begin sample slow through the resin column at 500 liter/24 hours (equivalent to 103 B.V./hr)

4) Take 50 ml aliquot from the effluent water at zero and 24 hours and analyze for chloroform section (6.6). Also analyze for glucose, glycine, acidic, neutral and basic compounds (Sections 6.2, 6.1, 6.4, and 6.3).

5) Elute with 3 x 150 ml 0.1N HCL in water and rinse with deionized water to a neutral pH. This step was added since it was necessary in lead concentration studies to remove lead. This eluant will be analyzed for acidic group compounds.

6) Elute with 3 x 150 ml distilled ether. An aliquot is taken for analysis of model compounds, and the remainder is concentrated for artifacts determination by GC/MS.

7) Elute with 3 x 150 methanol. An aliquot is taken for analysis of model compounds, and the remainder is saved for optional analysis by GC/MS

8) Elute with 3 x 150 ml o.1N HCL/methanol. Concentrate to dryness. Bring up with ether and take aliquots for the analysis of model compounds and artifacts determination by GC/MS.

9) Elute with 3 x 150 ml 0.1N HCL/ether and analyze as described in previous step.

10) Elute with 3 x 150 ml saturated HCL/methanol and analyze as described in previous step.

In order to evaluate the resin bank pilot study with respect to the oily colored residues previously found, the chemist involved in the concentration of the solvents for analysis by GC/MS made the following observations:

1) Ether eluants: Reagent blank was clear with no color, residue or film on the concentration tube. The resin blank eluant had small amount of brownish residue. This residue was dissolved again in ether.

2) 0.1N HCL/methanol eluants: Reagent blank was clear with no color or residue. The resin eluant had about 1 ml of black particles. This was diluted to 15 ml with methanol, then diluted to 1:10 for analysis by GC/MS.

3) 0.1N HCL/ether eluant: Reagent blank was clear with no color, but slight white film. The resin eluant had about 0.2-0.3 ml of brown to black residue. This residue was not soluble in ether, but methanol dissolved most of it.

4) Saturated HCL/methanol eluants: The Reagent blank was clear with no color, but the resin eluant had a clear yellowish color, but the resin eluant had a clear yellowish color. The 450 ml eluant was only concentrated to 100 ml.

The results of GC/MS analysis (Appendix F) for artifacts determination are tabulated in Table 46.

The reagent blank saturated HCL methanol and resin blank saturated HCL methanol were not analyzed by GC/MS due to their high acid content.

TABLE 46. RESULTS OF GC/MS ANALYSIS FOR ARTIFACTS DETERMINATION OF PILOT PLANT EXPERIMENT

Peak Number	Retention Time	Similarity Index	Compound	ug per g of dry resin
Ether Reagent Blank				
1	5.2	0.9757 0.9725	acetaldehyde diethyl - acetol 2-(2-ethoxyethoxy)ethanol	0.013
2	5.3	0.9713	ethyl acetate	0.210
3	6.4	0.9762	ethyl sec-butyl ether	0.006
4	6.6	--	none of the library hits were good matches	0.007
5	19.2	--	phthalate	
Ether Resin Blank				
1	5.4	--	polymethylpolysilozane (PMPs)	0.009
2	8.7	0.9761	hexanoic acid	0.012
3	9.0	--	PMPs *	0.020
4	9.4	--	PMPs	0.010
5	11.1	0.8451 0.7115	3-methyl-3-hexanol 2-ethyl-heptanoic acid	0.011
6	11.8	--	benzoic acid	0.162
7	12.1	0.9787 0.9786	1-(2-butoxyethoxy)ethanol 2-(2-butoxyethoxy)ethanol	0.046
8	12.9	--	PMPs	0.027
9	13.2	0.9730	diethylene glycol diacetate	0.021
10	14.0	0.9741	dibutyl orthoformate }	2.323 (both peaks combined)
11	14.05	cf. peak #10 (indistinquishable from it)		

(Continued)

TABLE 46. (Continued)

12	15.0	--	dimethyl phthalate	0.014
13	15.3	--	no good hits	0.064
14	16.2	--	diethyl phthalate	0.112
15	18.4	--	phthalate (possibly diisobutyl?)	0.053
16	19.1	--	dibutyl phthalate	0.020
17	19.5	00	PMPs	0.012
1	19.2	--	dibutyl phthalate	0.015
0.1 N HCl/Ether Reagent Blank				
1	19.2	--	dibutyl phthalate	0.015
0.1 N HCl / Ether Resin Blank				
1	4.9	0.9766	4-methyl-3-penten-3-one(mesityl oxide)	0.050
2	5.4	--	PMPs	1.879
3	5.4	--	PMPS	(both peaks)
4	6.1	0.8582	methyl sulfate	0.090
5	7.8	--	not identified (possibly ethyl sulfate?)	0.182
6	9.1	--	PMPs	7.712
7	10.2	--	not identified	0.034
8	10.5	--	not identified	0.093
9	11.5	--	PMPs	0.583
10	11.6	c.f. peak #9		1.120
11	12.1	--	not identified	0.047
12	13.5	--	PMPs	0.264
13	14.3	--	PMPs	2.303
14	15.1	--	PMPs	2.452
15	18.5	--	PMPs	0.272

(Continued)

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*PMPs is abbreviation for "polymethylpolysilozane"

TABLE 46. (Continued)

Peak Number	Retention Time	Similarity Index	Compound	ug per g of dry resin
0.1 N HCl/Ether Resin Blank (Continued)				
16	19.5	--	PMPs *	0.145
17	20.6	--	PMPs	0.048
0.1 N HCl/Methanol Reagent Blank				
1	5.6	--	PMPs	0.011
2	9.0	--	PMPs	0.479
3	11.5	--	PMPs	0.029
4	17.6	--	PMPs	0.016
5	17.7	--	PMPs	0.017
6	18.3	--	PMPs	0.043
7	18.3	--	PMPs	0.041
8	18.5	--	PMPs	0.082
9	19.2	--	PMPs	0.012
10	19.3	--	PMPs	0.010
11	19.4	--	PMPs	0.019
0.1 N HCl/Methanol Resin Blank				
1	4.7	0.9771 0.9754	4-methyl-3-penten-2-one(mesityl oxide) 3-hezen-2-one	13.088
2	5.5	--	PMPs	5.908
3	6.2	cf. FRN 19928, #4 (methyl sulfate)		10.2398
4	7.0	0.9758 0.9751 0.8151	2-isopropyl-1,3-dioxolane tetramethylsilane 2-n-propyl-1,3-dioxolane	1.487

(Continued)

TABLE 46. (Continued)

5	7.8	cf. FRN 19928, #5		3.566
6	8.0	0.9750 0.9750 0.9750	2,3-dimet-yl-2-pentanol 2,4-dimethyl-2-pentanol 2-methyl-2-hexanol	2.635
7	9.1	--	PMPs	7.461
8	11.6	--	PMPs	2.799
9	12.3	--	Not identified	0.884
10	13.6	--	PMPs	1.501
11	14.2	--	no good hits	1.001
12	18.5	--	PMPs	0.446
13	19.5	--	PMPs	0.410
0.1 N HCl/Ether Resin Blank Dissolved in Methanol				
1	4.7	cf. FRN 19933, #1		0.331
2	5.5	--	PMPs	0.492
3	6.2	cf. FRN 19928, #4		0.352
4	7.7	cf. FRN 19928, #5		0.150
5	7.9	cf. FRN 19933, #6		0.138
6	9.0	--	PMPs	0.205
7	11.4	--	PMPs	0.330
8	13.4	--	PMPs	0.124
9	17.4	--	PMPs	0.177
10	19.1	--	PMPs	0.053

---

[*] PMPs is abbreviation for "polymethylpolysilozane"

As can be seen in Table 46, many of the major peaks in the acidic eluant samples were polymethyl polysiloxanes (PMPS) that are believed to be artifacts from the column or septa. When a non-acidic solvent such as ether was analyzed, very few siloxane compounds were found.

It is important to note that at least two of the samples contained a compound identified by the library as methyl sulfate. This might suggest the presence of organic salts when the acidic eluants are concentrated, rather than inorganic salts. In general, when a compound was found in both the reagent and the resin blanks, the concentration of the compound was higher in the resin blank. The source of the PMPS compounds is not known, but one possible explanation could be the stripping of the column liquid phase by the acidic solvents.

8.2 PILOT PLANT STUDIES 1, 2 AND 3

The experimental work involved in pilot plant studies 1, 2 and 3 was basically the same as the resin blank pilot study. Twenty-one of the 22 model compounds were present in all three studies, but the inorganic salts were present in two studies, and the humic substances were included only in the last experiment. This order was chosen based on the possibility that the humic substances might not be desorbed 100%, therefore, altering the effectiveness of the resin in the adsorption of other model compounds.

The system was rinsed each time with water and ether followed by acetone and, finally, organic free water. During each run, the flow rate was measured to ensure constant flow operation.

The model compounds were added either in groups or as single standards. 2,4-dichlorobiphenyl, anthraquinone, stearic acid, and 5-chlorouracil were added in single standards. When stearic acid was added, some of it appeared on the surface as insoluble particles. This was corrected in pilot plant study 3 by adding a higher volume of less concentrated standard of stearic acid. Salts were added to the tank when it was being filled and when the tank's level reached 500 liters, it was mixed for 5 minutes for a homogeneous mixture. Mixing was also required when the model compounds were added, but this was kept to a minimum to prevent loss of volatile compounds.

Per EPA's suggestion, one liter of the influent water sample was taken (after addition of model compounds) and analyzed for extractable compounds. This was performed as a check for the concentration of standards used in spiking the 500 liter pilot plant experiments.

The tank and tubing used for the influent water was rinsed with approximately 2 liters of organic free water. This is the same procedure used in the reservoir washes for the bench scale studies, and is utilized in order to complete the mass balance calculations. This step was followed by a methylene chloride rinse to pick up any insoluble compounds. The methylene chloride rinse was added to the methylene chloride used in the extraction of the tank water rinse.

The desorption steps were performed in the columns three times with 150 ml of solvents as in the resin blank pilot plant study. The resin was shaken each time, then allowed to stand for 20-30 minutes before it was drained. Volumes were adjusted when necessary to take aliquots for different analyses. Internal standards were added immediately prior to analysis to eliminate the need for exact measurement of the volumes and compensation in sample size injection.

Table 47 shows the concentration and analytical scheme in the 500 liter pilot plant study.

As indicated in Table 47, the total mass of chloroform present is 25,000 ug or 50 ug/l. Therefore, it appears chloroform can be concentrated by the XAD-4 Quaternary resin on the average of 420-fold. In pilot plant study 1, the influent water shows that either chloroform was volatilized or tank water was not mixed well. Pilot plant study 2, the blank water, effluent water at zero hour, and the reservoir rinse show abnormally high chloroform concentrations that may be attributed to the organic free water system generation.

Glycine in Pilot Plant Study 1

This model compound was only analyzed during pilot plant study 1, since as shown in the bench-scale studies, the XAD-4 Quaternary resin in the OH^- form does not concentrate glycine. The results of the glycine analysis are shown in Table 49.

Glycine was analyzed using the fluorometric method by preparing a blank from the resin blank pilot plant study. An aliquot of the effluent water was spiked with all model compounds except glycine at the specified concentration levels. This technique represents the worst possible condition under which glycine could be analyzed and since 80.7% of glycine appeared in the effluent water, it is once again shown that glycine cannot be concentrated by the XAD-4 Quaternary resin

Humic Substances in Pilot Plant Study 3

The analyses of humic substances in the acidic eluants and the effluent water were performed by using a Bausch and Lomb spectrophotometer and a 5-cm length cell. The standards were prepared in 0.1N HCL/methanol at 10, 20, 30, and 40 ppm, while the aqueous standards were prepared at 500, 1000, and 2000 ppb. The results are shown in Table 50.

TABLE 47. ANALYTICAL SCHEME FOR 500 LITERS, PILOT STUDY

Model Compounds	Total Mass[3] (μg)	Eluant	Reservoir[1]	Aqueous Effluent
Quinaldic Acid	25,000	HPLC ion-pairing	HPLC ion-pairing	--
Trimesic Acid	25,000	HPLC ion-pairing	HPLC ion-pairing	--
2,4-Dichlorophenol	25,000	Cap. GC/FID	Cap. GC/FID	Ext$^{\underline{n}}$, Cap. GC-FID
Stearic Acid	25,000	Derivatization with diazo-methane, Capillary GC/FID	Derivitazation with diazo-methane, Capillary GC/FID	Extraction, derivitization with diazomethane, Capillary GC/FID
Humic substances	1,000,000	Spectrophometric	not necessary	Spectrophotometric
Glycine	25,000	--	--	Fluorometric
Furfural	25,000	Cap. GC/FID	Cap. GC/FID	Ext$^{\underline{n}}$, Cap. GC/FID
Quinoline	25,000	Cap. GC/FID	Cap. GC/FID	Ext$^{\underline{n}}$, Cap. GC/FID
Caffeine	25,000	Cap. GC/FID	Cap. GC/FID	Ext$^{\underline{n}}$, Cap. GC/FID
2,4,-Dichlorobiphenyl	25,000	Cap. GC/FID	Cap. GC/FID	Ext$^{\underline{n}}$, Cap. GC/FID
2,2',5,5'-Tetrachlorobiphenyl	25,000	Cap. GC/FID	Cap. GC/FID	Ext$^{\underline{n}}$, Cap. GC/FID
BEHP	25,000	Cap. GC/FID	Cap. GC/FID	Ext$^{\underline{n}}$, Cap. GC/FID
1-Chlorododecane	2,500	Cap. GC/FID	Cap. GC/FID	Ext$^{\underline{n}}$, Cap. GC/FID
Biphenyl	25,000	Cap. GC/FID	Cap. GC/FID	Ext$^{\underline{n}}$, Cap. GC/FID
Isophorone	25,000	Cap. GC/FID	Cap. GC/FID	Ext$^{\underline{n}}$, Cap. GC/FID
Anthraquinone	25,000	Cap. GC/FID	Cap. GC/FID	Ext$^{\underline{n}}$, Cap. GC/FID
MIBK	25,000	Cap. GC/FID	Cap. GC/FID	Ext$^{\underline{n}}$, Cap. GC/FID
2,6-Di-tert-butyl-4-methylphenol	25,000	Cap. GC/FID	Cap. GC/FID	Ext$^{\underline{n}}$, Cap. GC/FID
Phenanthrene	500	Cap. GC/FID	Cap. GC/FID	Ext$^{\underline{n}}$, Cap. GC/FID
Chloroform[2]	25,000	Packed Col. GC/EC	Packed Col. GC/EC	Packed Col. GC/EC
5-Chlorouracil	25,000	HPLC	HPLC	Ext$^{\underline{n}}$, HPLC
Glucose	25,000	--	--	Preserve, send to EPA

NOTE: [1] The reservoir was rinsed with methanol after passage of water through the resin. The methanol rinse required additional pretreatment in some cases prior to analyses.

[2] Deionized water was analyzed for chloroform.

[3] The influent water spiked with model compounds was analyzed for neutral extractable compounds by Cap. GC/FID in order to confirm amounts added.

TABLE 48. RESULTS OF CHLOROFORM IN PILOT PLANT STUDIES
(CHLOROFORM CONCENTRATION 50 ppb = 25,000 ug)

	Resin Blank	Pilot Plant Study 1	Pilot Plant Study 2	Pilot Plant Study 3
Blank Water	15.1 ppb	2.86 ppb	9.18 ppb	2.3 ppb
Reservoir Water After Spiking	No test	24.9 ppb	43.9 ppb	41.8 ppb
Effluent Water at Zero Hour	No test	ND	7.11 ppb	ND
Effluent Water After 24 hours	515 ug	6175 ug	12300 ug	8900 ug
Reservoir Rinse	ND	ND	5550 ug	1900 ug
Ether Eluant	3170 ug	8700 ug	10600 ug	9000 ug

TABLE 49. RESULTS OF GLYCINE IN PILOT PLANT STUDY NO. 1

	Study No. 1 Pilot Plant	Total % Mass Balance
Blank water	N.D. ppb	--
Reagent blank	N.D. ppb	--
Effluent water	40.35 ppb	80.7
Reservoir rinse	N.D. ppb	--

TABLE 50. RESULTS OF HUMIC SUBSTANCES IN PILOT PLANT STUDY NO. 3

Sample	Humic Substances	% Total Mass Balance
Effluent Water	450,000 ug	45
0.1 N HCl/ether	23,100 ug	2.31
0.1 N HCl/methanol	51,000 ug	5.10
0.1 N HCl/methanol	333,088 ug	33.3
Satd. HCl/methanol		
Total	857,188 ug	85.7

5-Chlorouracil (HPLC Analysis)

As shown in Table 51, precision and accuracy of the 5-chlorouracil recovery in 0.1N HCL/methanol is good, but a surprisingly high concentration of 5-chlorouracil in the neutral water suggests that this compound could very well be desorbed with neutral water. This phenomenon was never experimented in the bench-scale studies.

As mentioned previously, one liter of tank water was withdrawn after spiking and mixing in order to verify the concentration of each compound used in the standard spiking solutions. This verification, of course, could only be performed for methylene chloride extractable compounds. Table 52 shows the results of three such samples.

The recoveries were particularly poor for some of the neutrals, notably 1-Cl dodecane, anthraquinone, and BEHP. The poor recoveries were probably due to poor mixing since these compounds are less soluble than others. The extraction efficiency of these compounds in the spiked water (pre-resin) was lower than that observed in the past. Therefore, it was decided to follow EPA's suggestion that the concentration of spiking mixes should be verified if poor recoveries were observed.

Fresh standards were prepared from the pure material for 1-Cl dodecane, anthraquinone, and BEHP. Standard mix 830 was used to verify the concentration of another solution (Mix 824) which was prepared from the spiking mix. An additional sample of anthraquinone standard was analyzed because a fresh spiking standard had to be prepared for pilot plant study 3.

The results of the verification of these three compounds are shown below:

1) Mix 830 (used to check spiking mix)

	r. t.	Conc.	Area	RF*
1-Chlorododecane	18.24	2.5 ppm	1199	2.10
Anthraquinone	24.45	25.0	11490	2.19
BEHP	29.39	25.1	18110	1.40
n-Pentadecane	18.58	20.0	20170	--

$$*RF_s \quad \frac{A(is) \times C(s)}{A(s) \times C(is)}$$

2) Mix 824 (prepared from spiking mix)

	r. t.	Area	Presumed Conc.	Actual Conc.*
1-Chlorododecane	18.24	1085	2.5	2.49
Anthraquinone	24.45	13290	25.6	31.9
BEHP	29.39	12330	25.2	18.9
n-Pentadecane	18.58	18270	--	20

TABLE 51. RESULTS OF 5-CHLOROURACIL IN PILOT PLANT STUDIES

Sample	Resin Blank	Pilot Plant Study No. 1	Pilot Plant Study No. 2	Pilot Plant Study No. 3
Neutral water eluant	--	3737 ug	9800 ug	5874 ug
Reservoir rinse	62 ug	60 ug	60 ug	61 ug
0.1 N HCl/ methanol	272 ug	6444 ug	8082 ug	7953 ug
0.1 N HCl/ H_2O	284 ug	1788 ug	2896 ug	2484 ug

TABLE 52. EXTRACTION RESULTS OF PILOT PLANT TANK WATER AFTER SPIKING

Compound	Total Mass (ug)				Percent Extraction eff. (using avg. of 3)
	Spike Level	Pilot Plant Study No. 1	Pilot Plant Study No. 2	Pilot Plant Study No. 3	
MIBK	25000	18516	17506	17423	71.3
Furfural	25000	20466	18488	19237	77.6
Isophorone	25000	18308	17139	17871	71.1
Quinoline	25000	13944	12434	14063	53.9
Biphenyl	25000	16096	15585	16206	63.8
1-Chlorododecane	25000	272	271	610	15.4
BHT	25000	15250	15426	12681	57.8
2,4'-Dichlorobiphenyl	25000	13314	10139	14612	50.8
Phenanthrene	500	248	223	255	48.4
Caffeine	25000	7710	5589	7198	27.3
2,5,2',5'-Tetrachlorobiphenyl	2500	1572	1688	2105	71.5
Anthraquinone	25000	11218	10574	11015	43.7
BEHP	25000	7420	7282	7906	30.1

3) Standard 825-1 (anthraquinone) - Prepared from 825, which was also used for spiking in pilot plant study 3 only.

	r. t.	Area	Presumed Conc.	Actual Conc.**
1-Chlorododecane	24.45	10310	25.1	14.7
n-Pentadecane				

$$\text{**Conc.} = \frac{A_s \times C_{is} \times RF}{A_{is} \times \text{Volume (mls)}}$$

The results show that the 1-chlorododecane concentration in the spiking mix was actually what it purported to be. However, the concentration of BEHP was = 75% of what it was supposed to be. In one case, the actual anthraquinone concentration was higher than it was supposed to be, while in the other case it was lower. Therefore, the percent recoveries may be unrealistically high or low for those two compounds. None of the data has been corrected to reflect these conclusions.

The above verification still would not explain 30.1% recovery of BEHP compared to more than 80% in previous extraction experiments. The same unknown source of error also holds for 1-chlorododecane and anthraquinone.

The analytical results for the 14 model compounds amenable to GC/FID analysis are shown in Table 53. For complete mass balance determinations, the ether and methanol eluant solvents were analyzed both with and without concentration. The effluent water and the reservoir rinse were only analyzed for base/neutral extractables.

Quinaldic Acid (HPLC Analysis) (Conc. = 50 ppb or 25,000 ug)

As can be seen in Table 54, quinaldic acid was recovered at between 96-120%. The HPLC analysis of quinaldic acid in bench-scale studies had shown an interfering peak which is believed to cause higher than 100% recovery of this compound. It is interesting to note that the quinaldic acid mass balance in pilot plant study 3 is the lowest, and as can be seen later in the discussion of trimesic acid, the humic substances have definitely caused the lower recovery. This means that quinaldic acid was either not absorbed as well in the presence of humic substances or the desorption could not be as complete since 15% of the humic substances could not be accounted for. It should be mentioned again that quinaldic acid in the effluent water at 50 ppb could not be successfully performed. Therefore, the effluent water was not analyzed for this compound.

TABLE 53. SUMMARY OF MASS BALANCE OF 14 MODEL COMPOUNDS AMENABLE TO GC/FID ANALYSIS IN THREE PILOT PLANT STUDIES

	Resin Blank Study	Pilot Plant Study No. 1	Pilot Plant Study No. 2	Pilot Plant Study No. 3
MIBK - μg recovered in:				
Ether eluant (unconcentrated)		8617	7027	6393
MeOH eluant (unconcentrated)				
Eff. H_2O - B/N extract				
Res. Wash Water - B/N extract				
Ether eluant (concentrated 10→1)				
MeOH eluant (concentrated 10→1)				
	$\overline{\text{ND}}$	$\approx\overline{8617}$	$\approx\overline{7027}$	$\approx\overline{6390}$
Furfural - μg recovered in:				
Ether eluant (unconcentrated)		(see ether concentrated 10→1)		
MeOH eluant (unconcentrated)				
Eff. H_2O - B/N extract		12440	13815	12587
Res. Wash Water - B/N extract				
Ether eluant (concentrated 10→1)		967	581	140
MeOH eluant (concentrated 10→1)				
	$\overline{\text{ND}}$	$\approx\overline{13400}$	$\approx\overline{14400}$	$\approx\overline{12700}$
Isophorone - μg recovered in:				
Ether eluant (unconcentrated)		16613	13047	13800
MeOH eluant (unconcentrated)				
Eff. H_2O - B/N extract		2663(?)	3085	3089
Res. Wash Water - B/N extract		11	8	8
Ether eluant (concentrated 10→1)				
MeOH eluant (concentrated 10→1)				
	$\overline{\text{ND}}$	$\approx\overline{19300}$	$\approx\overline{16100}$	$\approx\overline{16900}$
2,4-Cl_2phenol - μg recovered in:				
Ether eluant (unconcentrated)	49	10162	8661	6550
MeOH eluant (unconcentrated)		1989(?)	2938(?)	5537
Eff. H_2O - B/N extract				
Res. Wash Water - B/N extract		2	1	
Ether eluant (concentrated 10→1)				
MeOH eluant (concentrated 10→1)				
	$\overline{49}$	$\approx\overline{12200}$	$\approx\overline{11600}$	$\approx\overline{12100}$

(Continued)

TABLE 53. (Continued)

	Resin Blank Study	Pilot Plant Study No. 1	Pilot Plant Study No. 2	Pilot Plant Study No. 3
Quinoline - μg recovered in:				
Ether eluant (unconcentrated)		7740	6841	5419
MeOH eluant (unconcentrated)				
Eff. H_2O - B/N extract				
Res. Wash Water - B/N extract		6	4	
Ether eluant (concentrated 10→1)				
MeOH eluant (concentrated 10→1)				
	ND	≈7750	≈6850	≈5420
Biphenyl - μg recovered in:				
Ether eluant (unconcentrated)	0.2	15647	12957	10066
MeOH eluant (unconcentrated)		1459	2163	3028
Eff. H_2O - B/N extract				
Res. Wash Water - B/N extract		21	18	29
Ether eluant (concentrated 10→1)				
MeOH eluant (concentrated 10→1)				
	<1	≈17100	≈15100	≈13100
1-Chlorododecane - μg recovered in:				
Ether eluant (unconcentrated)	4(?)	853	2174	772
MeOH eluant (unconcentrated)				274(?)
Eff. H_2O - B/N extract				
Res. Wash Water - B/N extract		6	4	7
Ether eluant (concentrated 10→1)				
MeOH eluant (concentrated 10→1)				
	4(?)	859	≈2180	≈1050

(Continued)

TABLE 53. (Continued)

	Resin Blank Study	Pilot Plant Study No. 1	Pilot Plant Study No. 2	Pilot Plant Study No. 3
BHT - μg recovered in:				
Ether eluant (unconcentrated)	0.5	13111	10576	6995
MeOH eluant (unconcentrated)		3044	1372	4265
Eff. H_2O - B/N extract				
Res. Wash Water - B/N extract		22	25	25
Ether eluant (concentrated 10→1)				
MeOH eluant (concentrated 10→1)				
	<1	≈16200	≈12000	≈11300
2,4'-Cl_2biphenyl - μg recovered in:				
Ether eluant (unconcentrated)		13704	8836	9453
MeOH eluant (unconcentrated)		1378	1197	2273
Eff. H_2O - B/N extract				
Res. Wash Water - B/N extract		51	45	66
Ether eluant (concentrated 10→1)				
MeOH eluant (concentrated 10→1)				
	ND	≈15100	≈10100	≈11800
Phenanthrene - μg recovered in:				
Ether eluant (unconcentrated)		(see ether concentrated 10→1)		
MeOH eluant (unconcentrated)				
Eff. H_2O - B/N extract				
Res. Wash Water - B/N extract		8(?)	6	3
Ether eluant (concentrated 10→1)		255	277	220
MeOH eluant (concentrated 10→1)				
	ND	263	283	223

(Continued)

TABLE 53. (Continued)

	Resin Blank Study	Pilot Plant Study No. 1	Pilot Plant Study No. 2	Pilot Plant Study No. 3
Caffeine - μg recovered in:				
Ether eluant (unconcentrated)		(see ether concentrated 10→1)		
MeOH eluant (unconcentrated)				
Eff. H_2O - B/N extract		6053	5740	7021
Res. Wash Water - B/N extract		13	5	3
Ether eluant (concentrated 10→1)		206	187	139
MeOH eluant (concentrated 10→1)				
	ND	≈6270	≈5930	≈7160
2,5,2',5'-Cl_4biphenyl - μg recovered in:				
Ether eluant (unconcentrated)	11	1176	1097	718
MeOH eluant (unconcentrated)				
Eff. H_2O - B/N extract				
Res. Wash Water - B/N extract		42	19	
Ether eluant (concentrated 10→1)				
MeOH eluant (concentrated 10→1)				
	11	≈1220	≈1120	718
Anthraquinone - μg recovered in:				
Ether eluant (unconcentrated)	8	12719	10054	9879
MeOH eluant (unconcentrated)		504	1038	1455
Eff. H_2O - B/N extract				
Res. Wash Water - B/N extract		63	35	30
Ether eluant (concentrated 10→1)				
MeOH eluant (concentrated 10→1)				
	8	≈13300	≈11100	≈11400
BEHP - μg recovered in:				
Ether eluant (unconcentrated)	5	5585	5712	3771
MeOH eluant (unconcentrated)				
Eff. H_2O - B/N extract		2799	4027	1054
Res. Wash Water - B/N extract		302	205	895
Ether eluant (concentrated 10→1)				
MeOH eluant (concentrated 10→1)				
	5	≈8690	≈9940	≈5720

TABLE 54. RESULTS OF QUINALDIC ACID IN PILOT PLANT STUDIES

	TOTAL MASS (ug) RECOVERED			
Sample	Resin Blank	Pilot Plant Study No. 1	Pilot Plant Study No. 2	Pilot Plant Study No. 3
Neutral Water Eluant	--	N.D.	770	N.D.
Reservoir rinse	N.A.	139	141	124
0.1 N HCl/H_2O	N.D.	N.D.	N.D.	N.D.
0.1 N HCl/methanol	N.D.	27262	29310	23979

Trimesic Acid (HPLC Analysis)

A very good mass balance of 75 and 93% total recovery was obtained in pilot plant studies 1 and 2 (Table 55). This suggests that the inorganic salts reduced the adsorption capacity of the XAD-4 Quaternary resin. This phenomenon has been a very difficult theory to prove in the laboratory.

The presence of humic substances caused a drastic reduction in the total recovery of trimesic acid in pilot plant study 3. Trimesic acid was recovered at 22.2% when humic substances were present with all of the other model compounds in pilot plant study 3.

Stearic Acid

In pilot plant studies 1 and 2, the stearic acid standard was spiked as a single compound, and it was observed that stearic acid was precipitating out (Table 56). The mixing, or the rate of the stearic acid addition, was independent of its solubility. In order to correct this phenomenon, it was decided to reduce the concentration of the standard solution and increase the volume. This was successfully performed in pilot plant study 3.

It was hoped that stearic acid would be recovered in the reservoir rinse or the effluent water, but only in pilot plant study 3, 30% recovery was accounted for. Therefore, the effect of salts and humic substances cannot be compared in respect to the stearic acid compound. It is important to note that stearic acid, being a straight chain carboxylic acid, was not adsorbed as well as other acidic compounds, and the major percentage of it was found in the effluent water.

2,4-dichlorophenol

2,4-dichlorophenol (Table 57) is desorbed in ether, methanol, acidic methanol, and acidic ether eluants (see Table 53 for ether and methanol eluants). Total recovery of 53 to 67% in the three pilot plant studies is less than expected compared to some earlier bench-scale experiments. Interestingly enough, the highest recovery was in pilot plant study 3 where the humic substances are present, but the differences in recoveries are not substantial enough to draw any concrete conclusions regarding the effect of humic substances on the concentration of 2,4-dichlorophenol.

1) Furfural
2) Isophorone
3) Caffeine
4) BEHP

TABLE 55. RESULTS OF TRIMESIC ACID IN PILOT PLANT STUDIES

	Total Mass Recovered (ug)			
Sample	Resin Blank	Pilot Plant Study No. 1	Pilot Plant Study No. 2	Pilot Plant Study No. 3
Neutral water eluant	--	N.D.	N.D.	N.D.
Reservoir Rinse	N.A.	N.D.	N.D.	N.D.
0.1 N HCl/H_2O	N.D.	N.D.	980	40
0.1 N HCl/methanol	N.D.	18913	22283	5543

TABLE 56. RESULTS OF STEARIC ACID IN PILOT PLANT STUDIES

	Total Mass Recovered (ug)			
Sample	Resin Blank	Pilot Plant Study No. 1	Pilot Plant Study No. 2	Pilot Plant Study No. 3
0.1 N HCl/ether	N.D.	N.D.	N.D.	N.D.
0.1 N HCl/Methanol	N.D.	N.D.	N.D.	408
Effluent water	N.D.	N.D.	N.D.	5521
Reservoir rinse	N.D.	N.D.	N.D.	216
0.1 N HCl/H_2O	2	13	13	14
Neutral Water eluant	2	16	9	1959

TABLE 57. RESULTS OF 2,4 DICHLOROPHENOL IN PILOT PLANT STUDIES

Sample	Resin Blank	Pilot #1	Pilot #2	Pilot #3
0.1 N HCl/methanol	N.D.	1974	1489	3657
0.1 N HCl/Ether	N.D.	614	261	875
Effluent Water	N.D.	N.D.	N.D.	N.D.
Neutral Water eluant	N.D.	N.D.	N.D.	N.D.
Reservoir rinse	N.D.	N.D.	N.D.	N.D.
0.1 N HCl/H_2O	N.D.	N.D.	N.D.	N.D.

Therefore, if the extraction efficiencies shown in Table 9 are used, the following mass balance for these four compounds can be obtained:

Compound	Pilot Plant Study 1	Pilot Plant Study 2	Pilot Plant Study 3
Furfural	96.0%	104.6%	93.8%
Isophorone	83.9%	72.4%	75.5%
Caffeine	39.9%	37.8%	45.8%
BEHP	37.2%	40.5%	23.8%

Furfural's mass balance is improved to near perfect while isophorone is well within range, but the extraction correction for caffeine and BEHP did not improve much.

The mass balance for each compound or total recovery can be viewed in two ways. One is a comparison within the pilot plant studies for the evaluation of the effect of the inorganic salts and the humic substances. The second method is to compare the mass balance results in the pilot plant studies to the bench-scale experimental results performed at 48 B.V./hr flow rate.

A) Comparison of pilot plant studies

	Salt Effect	Humics Effect	Precision and Accuracy	Mass Balance	50-fold Conc.
MIBK	None	None	A	L	A
Furfural	None	None	A	E	NA
Isophorone	None	None	A	G	A
2,4-dichlorophenol	None	None	A	G	A
Quinoline	None	None	A	L	A
Biphenyl	None	None	A	M	A
1-chlorododecane	Yes	None	A	L	A
BHT	Yes	None	A	M	A
2,4'-dichlorobiphenyl	Yes	None	A	M	A
Phenanthrene	None	None	A	M	A
Caffeine	None	None	A	L	NA
2,5,2',5'-tetrachlorobiphenyl	None	Yes	A	M	A
Anthraquinone	None	None	A	M	A
BEHP	None	Yes	A	L	A
Chloroform	Yes	None	NA	G	A
Stearic Acid	ND	NS	--	--	NA
Glycine	NS	NS	--	G	NA
5-chlorouracil	Yes	None	A	M	A
Quinaldic Acid	None	None	A	E	A
Trimesic Acid	None	Yes	A	G	A
Glucose	NS	NS	NS	--	NA

NOTE: ND = Not Dissolved
NS = Not Studied
A = Acceptable
NA = Not Acceptble
L = Low
M = Medium
E = Excellent
G = Good

One of the major objectives of this project (that is to concentrate the 22 model compounds 50-fold) has been achieved for 17 of the compounds. As can be seen from the above pilot plant results, furfural, caffeine, stearic acid, glycine, and glucose could not be concentrated 50-fold. But the mass balances, for example, for furfural and glycine were satisfactory. However, Table 58 indicates that the recoveries of MIBK, quinoline, 1-chlorododecane, 2,6-ditert-butyl-4-methyl-phenol, 2,4' dichlorabiphenyl, phenathrene, caffeine, 2,5,2',5'-tetrachlorobiphenyl, anthraquinone, BEHP, stearic acid, and trimesic acid are below 50% in pilot plant study 3 which most probably represents an actual water sample.

B) Comparison of pilot plant studies to bench scale studies in presence of humic substances at 48 B.V./hr.

In bench scale studies, better mass balances were obtained and compounds such as quinoline, 1-chlorododecane, caffeine, and BEHP had higher concentrations. Methyl isobutyl ketone, however, showed close to zero mass balance, but an acceptable 50-fold concentration was obtained in the pilot plant studies. This semi-volatile compound had shown variances in several bench-scale experiments due to its loss during concentration of the ether eluant. Caffeine, which was successfully concentrated 50-fold in the bench-scale studies, was one of the surprising compounds to show low total recovery and only between 3-5 fold concentration. Finally, humic substances showed better than 50-fold concentration in the saturated HCL/methanol eluant, but 45% of humics were found in the effluent water. In bench-scale studies, the humic substances were recovered mostly in the acidic solvents.

With respect to the acidic compounds, trimesic acid and 5-chlorouracil, which had no recovery in the bench-scale experiment, showed acceptable 50-fold concentration and good to medium mass balance. Stearic acid, due to its low solubility and lack of an acceptable analytical technique, has been a difficult compound to evaluate. Unfortunately, only one set of data was obtained in the pilot plant studies which shows again that the XAD-4 Quaternary resin is not a good choice of resin for the concentration of stearic acid from water. Quinaldic acid and 2,4-dichlorophenol were both concentrated better than 50-fold, but showed less total recovery in the pilot plant studies as compared to the bench-scale studies.

TABLE 58. SUMMARY OF MASS BALANCE OF ALL MODEL COMPOUNDS IN ALL PILOT STUDIES

	Amount Spiked (μg)	Resin Blank μg	Pilot Plant Study No. 1		Pilot Plant Study No. 2		Pilot Plant Study No. 3	
			μg	Percent	μg	Percent	μg	Percent
MIBK	25,000		8620	34.5	7030	28.1	6390	25.6
furfural	25,000		13400	53.6	14400	57.6	12700	50.8
isophorone	25,000		19300	77.2	16100	64.4	16900	67.6
2,4-dichlorophenol*	25,000	49	14700	59.0	13400	53.4	16600	66.5
quinoline	25,000		7750	31.0	6850	21.4	5420	21.7
biphenyl	25,000	<1	17100	68.4	15100	60.4	13100	52.4
1-chlorododecane	2,500	4	859	34.4	2180	87.2	1050	42.0
2,6-di-tert-butyl-4-methyl phenol	25,000	<1	16200	64.8	12000	48.0	11300	45.2
2,4'-dichlorobiphenyl	25,000		15100	60.4	10100	40.4	11800	47.2
phenanthrene	500		263	52.6	283	56.6	223	44.6
caffeine	25,000		6270	25.1	5930	23.7	7160	28.7
2,5,2',5'-tetrachlorobiphenyl	2,500	11	1220	48.8	1120	44.8	718	28.7
anthraquinone	25,000	8	13300	53.2	11100	44.4	11400	45.6
BEHP	25,000	5	8690	34.8	9940	39.8	5720	22.9
chloroform	25,000	3685	14875	59.5	28450	113.8	19800	79.2
stearic acid	25,000	2	29	<1	22	<1	8120	32.5
glycine	25,000	N.A.	20200	80.7	N.A.	N.A.	N.A.	N.A.
humics	1,000,000	--	N.A.	N.A.	N.A.	N.A.	857,000	85.7
5-chlorouracil	25,000	618	12000	48.0	20800	83.2	16400	65.6
quinaldic acid HPLC	25,000		27400	109.6	30200	120.8	24100	96.4
trimesic acid	25,000		18900	75.6	23300	93.1	5580	22.3

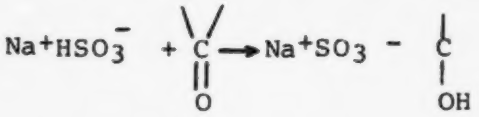
*These totals are sums of μg found in neutrals analysis for 2,4 DCP and acids analysis for 2,4 DCP (all GC cap FID results)

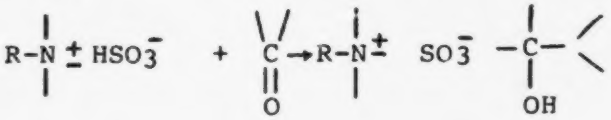
N. A. = Not analyzed

SECTION 9

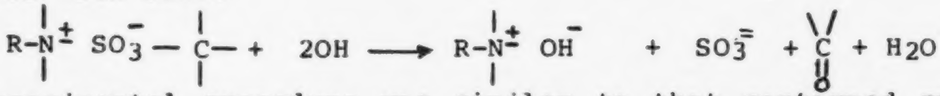
XAD-4 QUATERNARY RESIN (BISULFITE FORM)

XAD-4 Quaternary amine resin was evaluted in the bisulfite form. The basis for this work was the theory that bisulfite addition of compounds containing carbonyl groups might be possible in a manner analogous to those formed in synthetic organic chemistry, for example:





After concentration of the carbonyl compounds on the resin, they are desorbed with base.



The experimental procedure was similar to that performed previously on the XAD-4 Quaternary resin (OH^-), with important modifications, however. The resin was converted to the bisulfite form by passing three 25 ml portions of 2M $NaHSO_3$ through the resin. Compounds were desorbed from the resin by passing two portions (25 and 10 ml) of 1N NaOH in isopropanol followed by two 10 ml portions of pure isopropanol through the column.

Furfural and glucose were studied by this procedure. The results of these studies are summarized in Table 59.

It is interesting to compare these results with those obtained for the same compounds on the XAD-4 Quaternary resin (OH^-). For furfural, the behavior of the two resins was very similar [56.4% average recovery from resin eluant on XAD-4 Quaternary resin (OH) as compared with 55.1% average recovery from resin eluant on XAD-4 Quaternary resin (HSO_3^-)].

For glucose, only the aqueous effluent was analyzed and, based on these results (64.3% recovered from water), it appears that the resin is not effective in concentrating glucose from water.

In summary, while the XAD-4 Quaternary resin (HSO_3^-) shows the potential for improving separation/concentration of compounds containing carbonyl group(s), the data do not indicate any significant improvement over the XAD-4 Quaternary resin (OH^-).

TABLE 59. XAD-4 QUATERNARY (HSO_3-FORM)
ELUTION BY 1.0N NaOH IN ISOPROPANOL

Compounds		Percent Recovered from Resin Eluant	Percent Recovered From Water	Percent Recovered From Reservoir	Total Percent Recovered
Furfural	A	51.5	8.8	Not analyzed	60.3
52.4 μg/l	B	60.1	11.8	Not analyzed	71.9
	C	53.8	7.1	Not analyzed	60.9
Glucose	A	Not analyzed	71.1	Not analyzed	71.1
	B	Not analyzed	39.4	Not analyzed	39.4
	C	Not analyzed	84.0	Not analyzed	84.0

Work was continued on the bisulfite form of the XAD-4 anionic resin to determine whether this resin would be effective for the concentration of aldehydes. Furfural and glucose were studied again by adding these compounds to salted water at concentrations of 49.6 ug/l and 10.07 mg/l, described in the previous experiment, except that 0.5% v/v $H_2SO_4$was used as the eluant. Table 60 presents the results of the second experiment.

While the previous experiment with the XAD-4 Quaternary resin (HSO_3^-) was not conclusive, this experiment clearly shows neither glucose nor furfural is effectively adsorbed to the resin under the conditions used. The alternative desorption technique had no influence on the overall result of this experiment. The strikingly different result for furfural in this experiment as compared with those obtained in the first experiment indicates the difficulty of working with this compound, which appears to be unstable in water.

TABLE 60. XAD-4 QUATERNARY (HSO_3- FORM) ELUTION BY 0.5% H_2SO_4 IN WATER

Compounds		Percent Recovered from Resin Eluant	Percent Recovered from Water	Total Percent Recovered
Glucose	A	Not analyzed	91	91
	B	Not analyzed	116	116
	C	Not analyzed	101	101
Furfural	A	4.8	92.7	97.5
	B	4.8	97.8	102.6
	C	6.3	71.9	78.2

SECTION 10

XN-1010 RESIN

One experiment was performed using the XN-1010 resin, a strongly acidic cation exchange resin manufactured by Rohm and Haas. This resin was used to determine its effectiveness in concentrating selected bases. The basis for this work is the following hypothesized exchange mechanism:

$$R\text{-}SO_3^- \; H^+ \; + \; H_2N\text{-}R^1 \longrightarrow RSO_3^- \; N^+ \; H_3R^1$$

Elution of the adsorbed base is achieved with hydroxide:

$$RSO_3^- \; N^+ \; H_3R^1 \; + \; NaOH \longrightarrow RSO_3^- \; NA^+ \quad +NH_2R \; + \; H_2O$$

The specific procedure for desorption includes passing 1 bed volume of 2N NaOH followed by 4 bed volumes of methanol through the resin.

Experimental results for caffeine, 5-chlorouracil and glycine are summarized in Table 61. These results do not show any significant separation/concentration of caffeine or 5-chlorouracil. Glycine was found in only a small percentage of the amount added.

TABLE 61. XN-1010 RESIN

Model Compounds		Percent Recovered From Resin Eluant	Percent Recovered From Water	Percent Recovered From Reservoir	Total Percent Recovered
Caffeine 10.1 mg/l	A	Not analyzed	73.6	Not analyzed	73.6
	B	Not analyzed	66.8	Not analyzed	66.8
	C	Not analyzed	68.1	Not analyzed	68.1
5-chlorouracil 12.2 mg/l	A	Not analyzed	95.1	Not analyzed	95.1
	B	Not analyzed	70.9	Not analyzed	70.9
	C	Not analyzed	65.3	Not analyzed	65.3
Glycine 9.7 mg/l	A	Not analyzed	<10.0	Not analyzed	<10.0
	B	Not analyzed	46.4	Not analyzed	46.4
	C	Not analyzed	14.4	Not analyzed	14.4

SECTION 11

XE-340 RESIN

The XE-340 carbonaceous resin was evaluated to determine its effectiveness for the concentration of chloroform at 50 ug/l in salted water. Elution was with ether followed by methanol. The standard 1-liter resin evaluation procedure was used, except that elution was with 2 x 25 ml portions of distilled ether followed by 25 ml of methanol. The resin seemed to retain a substantial volume of the ether. The results of this experiment are summarized in Table 62.

Apparently, chloroform was strongly adsorbed on the resin and not effectively desorbed with the ether and methanol eluants. The resin also appeared to be somewhat fragile, and some "fine" due to "dusting" were observed when rinsing and packing the resin. This may have contributed to the interfering peaks observed in the GC analysis of the methanol fraction.

It does not appear that there are any advantages to the XE-340 resin for the concentration of chloroform. The XAD-4 Quaternary resin in the OH^- form has proved more effective, with none of the artifact problems. In addition, for volatile compounds (such as chloroform), there is always the possibility of identifying them separately through analysis, and testing the specific compounds separately for toxicity.

TABLE 62. CONCENTRATION OF CHLOROFORM ON XE-340

	Percent Recovered From Resin Eluant	Percent Recovered From Effluent	Total Percent Recovered
A	12.4	5.6	18.0
B	8.2	5.3	13.5
C	12.1	3.9	16.0

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Appendix A

Gas Chromatographic Conditions

Model Compound: Group I (Section 6.3)

Column: ______ **Capillary** X **Packed** ______

Length 30 **m**

Diameter 0.325 **i.d. mm**

Liquid Phase: DB-5 (SE-54)

Carrier Gas: H2

Inlet Pressure:

Flow Rate: ______ **ml/min** 20 **cm/sec**

Injection:

Split ______

Splitless X **Vent After** 0.5 min

Sample size 2 ul

Auxiliary or Make-Up Gas:

Type Gas: He

Flow Rate: 40 ml/min

Column Head Pressure: 10 psig

Detector: FID X ECD ____ NPD ____

Attenuation: 16 or 32

Flow Rate: ml/min Hydrogen: 30 Air: 300

Temperature: Detector 350 °C Inj 225 °C

Column Temperature:

Isothermal: yes ____ no X Temp. ____ °C

Program: yes X no ____

Initial 40 °C; Hold 4 min; program to 280 °C @ 10 °/min;

Hold 20 min; program to ____ °C @ ____ °/min; Hold ____.

Mass Spec. yes ____ no X

Mass Spec Ionization Current: uA @ 70eV

Source Temp ____ °C

Mass Range ____ amu

Scan time ____ sec

Appendix B

LIQUID CHROMATOGRAPHIC CONDITIONS

Model Compounds: 2,2',5,5' - Tetrachloroluphenly, BEHP, BHT, Isophorone, Anthraquinone, Biphenyl, 2,4 dichlorobiphenyl

Column: RP- 18 Length 20 cm I.D. 4.6 mm

Particle Size: 5 micron Phase: Reverse Phase

Mobile Phase: (A) Water (B) Acetomitrile

Flow Rate: 1.5 ml/min

Column Pressure: 165 Bar

Detector: UV

Wavelength: Sample 236 nm Reference 430 nm

Sample Size: 20 μl

Oven Temperature: 40 °C

Solvent Temperature: 40 °C

Gradient: yes X no ____ Wavelength Change: yes X no ____

Time	% B
0 min	60
13 min	86.2
17 min	95.0
22 min	95.0
25 min	60.0

Time	Wavelength
0 min	236 mm
4	254
8.50	225
14.50	276
18.00	225

Appendix C

LIQUID CHROMATOGRAPHIC CONDITIONS

Model Compounds: Quinaldric and Trimesic Acid

Column: $-NH_2$ Length 20 cm I.D. 4.6 mm

Particle Size: 5 micron Phase: Normal

Mobile Phase: (A) 0.005 M tetra-n-butyl Ammonium Phosphate/water (B) 15% Acetonitrile

Flow Rate: 1.0 ml/min

Column Pressure: 94 Bar

Detector: UV

Wavelength: Sample 236 nm Reference 430 nm

Sample Size: 150 µl

Oven Temperature: 40 °C

Solvent Temperature: 40 °C

Gradient: yes X no ___ Wavelength Change: yes ___ no X

Time	% B	Time	Wavelength
3.00	15		
5.00	50		
15.00	50		
16.00	15		
16.10	Stop		

a) Retention time effected by the sample size.
b) PH must be adjusted to 5 - 8 range.

Appendix D

LIQUID CHROMATOGRAPHIC CONDITIONS

Model Compounds: 5 - Chlorouracil

Column: RP.-8 Length 20 cm I.D. 4.6 mm

Particle Size: 5 micron Phase: Reverse Phase

Mobile Phase: (A) Water (B) 25% Acetonitrile

Flow Rate: 0.75 ml/min

Column Pressure: 85 Bar

Detector: UV

Wavelength: Sample 275 nm Reference 430 nm

Sample Size: 100 µl

Oven Temperature: 40 °C

Solvent Temperature: 40 °C

Gradient: yes ____ no X Wavelength Change: yes ____ no X

Time	% B	Time	Wavelength

Appendix E

Gas Chromatographic Conditions

Model Compound: Chloroform

Column: ______ **Capillary** ______ **Packed** X

. **Length** 2 **m**

Diameter 2 **i.d. mm**

Liquid Phase: 10% Squalane

Carrier Gas: 5% Methane/Argon

Inlet Pressure:

Flow Rate: 40 **ml/min** ______ **cm/sec**

Injection:

Split ______

Splitless ______ **Vent After** ______ min

Sample size 2 **ul**

Auxiliary or Make-Up Gas:

Type Gas: ______

Flow Rate: ______ ml/min

Column Head Pressure: ______ psig

Detector: FID ______ ECD X NPD ______

Attenuation: ______

Flow Rate: ______ Hydrogen: ______ Air: ______

Temperature: Detector 125 °C Inj 110 °C

Column Temperature:

Isothermal: yes X no ______ Temp. 65 °C

Program: yes ______ no ______

Initial ______ °C; Hold ______ min; program to ______ °C @ ______ °/min;

Hold ______ min; program to ______ °C @ ______ °/min; Hold ______.

Mass Spec. yes ______ no X

Mass Spec Ionization Current: uA @ 70eV

Source Temp ______ °C

Mass Range ______ amu

Scan time ______ sec

Appendix F

Gas Chromatographic Conditions

Model Compound: Chlorinated forming Compound by Chlorine

Column: ____ Capillary X Packed ____

· Length 30 m

Diameter 0.32 i.d. mm

Liquid Phase: DB -5 (SE-54)

Carrier Gas: H_2

Inlet Pressure:

Flow Rate: ____ ml/min 25 cm/sec

Injection:

Split ____

Splitless X Vent After 0.5 min

Sample size 2 ul

Auxiliary or Make-Up Gas:

Type Gas: ____

Flow Rate: ____ ml/min

Column Head Pressure: 12 psig

Detector: FID ____ ECD ____ NPD ____

Attenuation: ____

Flow Rate: ____ Hydrogen: ____ Air: ____

Temperature: Detector ____ °C Inj ____ °C

Column Temperature:

Isothermal: yes ____ no ____ Temp. ____ °C

Program: yes ____ no ____

Initial 40 °C; Hold 3 min; program to 300 °C @ 10 °/min;

Hold ____ min; program to ____ °C @ ____ °/min; Hold ____.

Mass Spec. yes X no ____

Mass Spec Ionization Current: uA @ 70eV

Source Temp 250 °C

Mass Range 45-450 amu

Scan time 1.0 sec

Appendix G

Gas Chromatographic Conditions

Model Compound: Chlorinated forming compounds by chlorine, and BEHP

Column: ____________ **Capillary** ____________ **Packed** X

Length 2 **m**

Diameter 4 **i.d. mm**

Liquid Phase: 1.5 % SP 2250 / 1.95% SP2401

Carrier Gas: 5% Methane/Argon

Inlet Pressure:

Flow Rate: 40 ml/min ________ cm/sec

Injection:

Split ________

Splitless ________ Vent After ________ min

Sample size 4 ul

Auxiliary or Make-Up Gas:

Type Gas: ____________

Flow Rate: ____________ ml/min

Column Head Pressure: __________ psig

Detector: FID _____ ECD X NPD _____

Attenuation: 32

Flow Rate: __________ Hydrogen: __________ Air: __________

Temperature: Detector 350 °C Inj 225 °C

Column Temperature:

Isothermal: yes X no _____ Temp. 200 °C

Program: yes _____ no _____

Initial _____ °C; Hold _____ min; program to _____ °C @ _____ °/min;

Hold _____ min; program to _____ °C @ _____ °/min; Hold _____.

Mass Spec. yes _____ no X

Mass Spec Ionization Current: uA @ 70eV

Source Temp _____ °C

Mass Range _____ amu

Scan time _____ sec

Appendix H

Gas Chromatographic Conditions

Model Compound: Stearic Acid
Column: ________ Capillary ________ Packed X
Length 2 m
Diameter 3 i.d. mm
Liquid Phase: SE - 30
Carrier Gas: He
Inlet Pressure:
Flow Rate: 40 ml/min ________ cm/sec
Injection:
Split ________
Splitless ________ Vent After ________ min
Sample size 2 ul
Auxiliary or Make-Up Gas:
Type Gas: ________
Flow Rate: ________ ml/min
Column Head Pressure: ________ psig
Detector: FID X ECD ____ NPD ____
Attenuation: 64
Flow Rate: ________ Hydrogen: 30 Air: 300
Temperature: Detector 300 °C Inj 200 °C
Column Temperature:
Isothermal: yes ____ no X Temp. ____ °C
Program: yes X no ____
Initial 190 °C; Hold 12 min; program to 250 °C @ 20 °/min;
Hold 10 min; program to ____ °C @ ____ °/min; Hold ____.
Mass Spec. yes ____ no X
Mass Spec Ionization Current: uA @ 70eV
Source Temp ____ °C
Mass Range ____ amu
Scan time ____ sec

Appendix I

Adsorption/Desorption Conditions

Experiment # 1 Page No. Report 61

Sample Volume: 1000 ml pH: 7.0

Model Compounds: Amount (ug)

Quinaldic Acid 49.1; Trimesic Acid 53.9; Stearic Acid 54.0;

Glycine 19740; Glucose 9800; Furfural 52.4; Chloroform 48.7;

Quinoline 48840; Caffeine 52300; 5-chlorouracil -; Biphenyl 596;

1-chlorododecane 502; BEHP 668; 2,4'-dichlorobiphenyl 404;

2,2', 5,5'-tetrachlorobiphenyl; 172; isophorene 500;

anthraquinone 50; MIBK 50,000; 2,4-dichlorophenol -; BHT 696;

phenanthrene -.

Salt Matrix: yes X no ____

Humic Acid: yes ____ no X Amt. Added ____ ug

Column Dimensions 13 cm x 10 mm i.d.

Resin Bed Volume: 10 cm^3

Flow Rate: 150 B.V./hr

Desorption Scheme

1)	0.1N HCl in H_2O	yes ____	no X	ml ____	Flowrate (B.V.) -
2)	ether	yes X	no ____	ml 50-150	Flowrate (B.V.) 150
3)	methanol	yes X	no ____	ml 50	Flowrate (B.V.) 150
4)	0.1N HCl/MeOH	yes ____	no X	ml ____	Flowrate (B.V.) -
5)	0.1N HCl/ether	yes X	no ____	ml 50	Flowrate (B.V.) 150
6)	Sat HCl/MeOH	yes ____	no X	ml ____	Flowrate (B.V.) -

Appendix J

LIQUID CHROMATOGRAPHIC CONDITIONS

Model Compounds: Trimesic Acid, Quinaldic Acid, and 2,4 - dichlorphenol

Column: RP.-18 Length 20 cm I.D. 4.6 mm

Particle Size: 5 micron Phase: Reverse Phase

Mobile Phase: (A) (B) Acetonitrile

Flow Rate: 1.0 ml/min

Column Pressure: 100 Bar

Detector: UV

Wavelength: Sample 235 nm Reference 430 nm

Sample Size: 25 μl

Oven Temperature: 40 °C

Solvent Temperature: 40 °C

Gradient: yes X no Wavelength Change: yes no X

Time min	% B	Time	Wavelength
0	33		
12.5	80		
13.5	33		
15.0	Stop		

Appendix K

LIQUID CHROMATOGRAPHIC CONDITIONS

Model Compounds: Caffeine, Furfural

Column: RP.-18 Length 20 cm I.D. 4.6 mm

Particle Size: 5 micron Phase: Reverse Phase

Mobile Phase: (A) Water (B) 33% Acetonitrile

Flow Rate: 1.0 ml/min

Column Pressure: 144 Bar

Detector: UV

Wavelength: Sample 150 nm Reference ________ nm

Sample Size: 40 μl

Oven Temperature: 40 °C

Solvent Temperature: ________ °C

Gradient: yes ______ no X Wavelength Change: yes ______ no X

Time	% B	Time	Wavelength

Appendix L

LIQUID CHROMATOGRAPHIC CONDITIONS

Model Compounds: Anthroquinone

Column: RP.-18 Length 20 cm I.D. 4.6 mm

Particle Size: 5 micron Phase: Reverse Phase

Mobile Phase: (A) Water (B) 65% Acetonitrile

Flow Rate: 1.5 ml/min

Column Pressure: 218 Bar

Detector: UV

Wavelength: Sample 225 nm Reference 430 nm

Sample Size: 150 µl

Oven Temperature: 40 °C

Solvent Temperature: 40 °C

Gradient: yes X no ____ Wavelength Change: yes ____ no X

Time	% B	Time	Wavelength
0	65		
12.5	95		
17.5	65		

Appendix M
Adsorption/Desorption Conditions

Experiment #__________ **Page No. Report**__________

Sample Volume: 1000 ml pH: 7.0

Model Compounds: Amount (ug)

Quinaldic Acid 50; Trimesic Acid 50; Stearic Acid 50;

Glycoine 50; Glucose 50; Furfural 50; Chloroform 50;

Quinoline 50; Caffeine 50; 5-chlorouracil 50; Biphenyl 50;

1-chlorododecane 5.0; BEHP 50; 2,4'-dichlorobiphenyl 50;

2,2', 5,5'-tetrachlorobiphenyl; 5.0; isophorene 50;

anthraquinone 50; MIBK 50; 2,4-dichlorophenol 50;

phenanthrene 1.0.

Salt Matrix: yes X no____

Humic Acid: yes X no ____ Amt. Added 2000ug

Column Dimensions 13 cm x 10 mm i.d.

Resin Bed Volume: 10 cm^3

Flow Rate: 48 B.V./hr

Desorption Scheme

1)	0.1N HCl in H_2O	yes ____	no X	ml ____	Flowrate (B.V.) ____
2)	ether	yes X	no ____	ml 150	Flowrate (B.V.) 48
3)	methanol	yes X	no ____	ml 50	Flowrate (B.V.) 48
4)	0.1N HCl/MeOH	yes X	no ____	ml 50	Flowrate (B.V.) 48
5)	0.1N HCl/ether	yes ____	no X	ml ____	Flowrate (B.V.) -
6)	Sat HCl/MeOH	yes X	no ____	ml 50	Flowrate (B.V.) 48